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APPLICATION NUMBER: *60/362,157*
FILING DATE: *March 06, 2002*
RELATED PCT APPLICATION NUMBER: *PCT/US03/06844*

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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

Express Mail Label No. EL565050438US

11135 U.S. PTO

U.S. PTO 60/362157 03/06/02

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TITLE OF THE INVENTION (500 characters max)

AN ELECTRICAL CONDITION MONITORING METHOD FOR POLYMERS

Direct all correspondence to: **CORRESPONDENCE ADDRESS**

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ENCLOSED APPLICATION PARTS ***(check all that apply)***

☑ Specification *Number of Pages* 14 ☐ CD(s), Number

☑ Drawing(s) *Number of Sheets* 6 ☑ Other (specify) Ref A, Ref B, Ref C

☐ Application Data Sheet. See 37 CFR 1.76

METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT

☑ Applicant claims small entity status. See 37 CFR 1.27.

☑ A check or money order is enclosed to cover the filing fees

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FILING FEE AMOUNT ($): $80.00

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☐ No.

☑ Yes, the name of the U.S. Government agency and the Government contract number are: Dept of Energy DE-FG02-01ER83153

Respectfully submitted,

SIGNATURE [signature]

Date 3/6/02

REGISTRATION NO. *(if appropriate)* 37466

TYPED or PRINTED NAME Kenneth S. Watkins, Jr.

Docket Number: BPW-06

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USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

PROVISIONAL APPLICATION COVER SHEET
Additional Page

PTO/SB/16 (02-01)
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Docket Number	BPW-06

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Number 2 of 2

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Docket No. BPW-06

Specification

Accompanying

Application for Grant of U. S. Letters Patent

INVENTORS: Kenneth S. Watkins, Jr., Shelby J. Morris, Ching Ping Wong, Shijian Luo, Daniel D. Masakowski

ASSIGNEE:

TITLE: AN ELECTRICAL CONDITION MONITORING METHOD FOR POLYMERS

This application resulted, in part, from research funded by the U. S. Department of Energy. Certain rights for any intellectual property resulting from this application may apply to the Government of the United States.

Field of the Invention

The present invention relates to methods and apparatus for determining deterioration and remaining life of polymeric material utilizing measured electrical quantities, and, more particularly, for determining mechanical properties and remaining life of a polymeric material by measurement of electrical resistivity of a conductive composite of the polymer.

Background of the Invention

(See Ref A, Watkins, K. S. "An Electrical Condition Monitoring Approach to Wire and Cable")

Summary of the Invention

An electrical condition monitoring method utilizes measurement of electrical resistivity of a conductive matrix disposed in a polymeric structure. The conductive matrix comprises a base polymer and a conductive filler. The method comprises a means for communicating the resistivity to a measuring instrument and a means to correlate resistivity of the conductive matrix of the polymeric structure with resistivity and mechanical properties of an accelerated-aged conductive matrix.

Brief Description of the Drawings

These and other features, aspects and advantages of the present invention will become better understood with regard to the following description, appended claims and accompanying drawings where:

FIG. 1 is a cross section of an electrical cable comprising a age sensor filament made of a conductive composite;

FIG. 2 is a cross section of an electrical cable comprising an age sensor filament co-extruded in an insulated conductor insulation and a cable jacket;

FIG. 3 is a schematic diagram of a means for measuring the resistivity of a conductive age sensor filament;

FIG. 4 is a perspective drawing of an electrical cable comprising a plurality of age sensors disposed in the cable jacket;

FIG. 5 is a perspective drawing of an electrical cable comprising an age sensor strip disposed in the cable jacket;

FIG. 6 is a perspective drawing of a plurality of age sensor assemblies utilizing an RFID to communicate resistivity to an external instrument; and

FIG. 7 is a perspective drawing of a a polymeric structure comprising a plurality of conductive composite age sensors disposed in the structure.

Description of the Preferred Embodiments

The following is a description of the preferred embodiments of a method for determining the degradation of a polymeric material by use of an electrical measurement.

Definitions: Although the term resistivity (electrical) is used throughout the specification, it is understood that conductivity, as the reciprocal of resistivity, can be substituted as a measurable electrical property by those skilled in the art.

The term conductive composite polymer, as used in this specification, is generally meant to include any conductive composite comprising a mixture of conductive particles in a polymer matrix or base, and may include additional fillers, additives and binders. This composite type conductive polymer is differentiated from intrinsically conductive polymers which posses electrically conductive properties without addition of conductive particles.

The method of the present invention (more fully described in Ref (A), Watkins, K. S., "An Electrical Condition Monitoring Approach for Wire and Cable", hereby incorporated by reference) utilizes measurement of an electrical property of a conductive composite to indirectly measure the aging or degradation effects on a polymeric material. In the

preferred embodiments, the conductive composite comprises conductive particles such as carbon black particles or metallic particles evenly dispersed or mixed in the polymeric material of interest. Degradation and aging effects which include chain scission and additional cross-linking will result in volumetric changes to the polymeric portion of the composite and will affect electrical properties such as the resistivity or conductivity of the composite.

Degradation and aging mechanisms of polymers are numerous and complex, but cross-linking of polymer chains, caused by thermal exposure, radiation exposure, and thermal-oxidative mechanisms has been shown in the literature to result in increased packing density of the polymer chains, resulting in densification and volumetric shrinkage. If conductive fillers are chosen which are relatively inert for the environments in which the composites are used and tested, the volume fraction of the filler will remain constant with degradation of the polymer matrix. The resulting volumetric shrinkage of the polymer matrix of a conductive composite results in an increase in the volume fraction of the conductive filler particles in the composite.

Changes in the volume fraction of conductive fillers can be detected by electrical measurements of the conductive composite. Specifically, the resistivity (or conductivity) provides a measure of the volume fraction of the conductive filler. Several of the mechanisms of resistivity change in conductive composites is more fully described in Ref. (B), Wong et al., Georgia Tech presentation of "An Electrical Condition Monitoring Approach for Wire and Cable Based on Conductive Polymer Composite" hereby incorporated by reference.

Resistivity measurements of conductive composites affords very high sensitivity to conductive filler volume fraction changes in conductive polymer composites as a result of polymer matrix shrinkage and densification. For example, the volumetric shrinkage of a polymer due to age-related cross-linking may be on the order of only a few percent over the useful life of the polymer. Selection of the conductive filler type and loading may result in several orders of magnitude of resistivity change due to the volumetric

shrinkage. This is especially the case if the conductive filler loading is chosen to be in the percolation zone as more fully described in Ref (B), Other aging mechanisms, such as loss of volatile components of the polymer during aging also result in an increase in the volume fraction of the conductive filler.

The high sensitivity of resistivity of a conductive polymer composite to volumetric shrinkage (or expansion) of the polymer matrix provides an amplified method useful in detecting an measuring the small changes in polymer volume fraction as a result of age-related degradation such as cross-linking of the matrix due to thermal, radiation, and thermal oxidative mechanisms. While direct measurements of volumetric shrinkage of the polymers would provide a quantitative means to detect degradation, this method is usually destructive for many applications, and requires laboratory analysis. Measurement of resistivity, although an indirect measurement of the volumetric shrinkage, provides a non-destructive, in-situ, measurement that is much more sensitive than can be done by normal laboratory measurements of volumetric shrinkage or density, and can be carried out with simple field equipment such as an ohmmeter or multimeter.

The amplifying effect of the conductive composite resistivity measurement approach allows measurement of volumetric or density changes smaller than that afforded by direct mechanical measurements. For example physical aging effects, such as relaxation of polymer chain networks of polymers below the glass transition temperature, and creep effects can be detected over short time intervals by resistivity measurements of conductive composites of the polymer. Preliminary aging tests (see Ref. (A), (B), and. (C), Watkins, K. S. "BPW, Inc. presentation of An Electrical Condition Monitoring Approach for Wire and Cable" hereby incorporated by reference) suggest that detection of natural aging effects over short time periods, such as days or weeks is possible by this method, where months or years would be required by conventional mechanical or chemical measurements such as elongation to break, and oxygen induction time (OIT) measurements.

Examples:

See references (A), (B), (C)

Use of resistivity data of polymeric composite materials could be used in several ways. For example, accelerated aging of a composite comprising a specific polymer and a given volume fraction of a conductive filler would result in a resistivity vs. time for the test temperature. Measurement of mechanical properties such as elongation to break or hardness as the composite is aged, would provide a relationship of the mechanical property to the resistivity for the composite. This relationship could be determined by the aging curve, such as that of Ref. (A, (B), and (C), showing the value of the mechanical property vs. resistivity. Or, the relationship could be expressed by a mathematical algorithm by curve fitting methods known in the art. By inclusion of base polymer samples (without conductive fillers) during the aging trial, the mechanical properties of the base polymer could be predicted by measurement of a representative sample of the conductive composite having the same base polymer.

By incorporating aging trials of a conductive composite at several temperatures, measuring resistivity and mechanical properties vs. aging time, Arrhenius methodology and/or time/temperature superposition known in the art could be used to predict remaining lifetime of the composite (or base polymer) as a function of aging temperature. In-situ measurement of the resistivity of a test or trial portion of the polymer having conductive filler could be used to verify the remaining life of the polymer and act as an indirect measurement of desired mechanical properties.

Physical aging affects of polymers could be modeled in a similar means by thermal processing a conductive composite, optionally in an inert gas environment, and measuring resistivity vs. mechanical properties such as volumetric shrinkage, density and creep properties.

FIG. 1 is a cross section of a multi-conductor cable having three insulated conductors, an outer cable jacket, and an age sensor filament disposed in the cabled conductors. In the

preferred embodiments, the age sensor filament "tracer" is a conductive composite comprising the conductor insulator polymer as the base polymer and a conductive filler such as carbon black. In other embodiments, the conductive composite utilizes a second polymer as the base polymer. In still other embodiments, the conductive composite utilizes metallic or metallic oxides as a the conductive filler. The sensor filament may be positioned at other locations in the cable such as outside the insulated conductors and inside the cable jacket.

Fig. 2 is an alternative embodiment of the cable of FIG. 1 utilizing a co-extruded age sensor tracer in the insulated portion of the insulated conductor, or co-extruded in the cable jacket. In the preferred embodiments, the preferred embodiments, the base polymer of the senor tracers is the same polymer as the insulated conductor or jacket. In other embodiments, a different base polymer is utilized.

FIG. 3 is a schematic of a method of monitoring the resistivity of the age sensor 303 of cable 301. Age sensor filament 303 is distributed along the cable and disposed, for example, along the insulated conductors 305. A second element 303A, is disposed along the length of cable 301inside jacket 307. Second element 303A may be another age sensor filament similar to age sensor filament 303, or it may be an insulated or non-insulated conductor such as a metallic conductor. Shunt 309 connects age sensor 303 and second element 303A to form a series-connected loop 311 which functions as an electrical age sensor for the cable. Age sensor loop 311 is connected by conductors 313 to terminal box 315. A resistance-measuring instrument, such as ohmmeter 317 measures the resistance of age sensor loop 311 at terminal box 315.. By monitoring resistance (or resistivity calculated from the sensor dimensions) changes in age sensor loop 311 and comparing the results to accelerated aged conductive composites and insulation base polymers, the material properties such as elongation-at-break of the insulation polymers may be determined.

In other embodiments ohmmeter 317 connects directly to age sensor 303 and second element 303A.

FIG. 5 is a perspective drawing of an alternative method of monitoring cable condition. Cable 401 comprises a plurality of condition or age sensors 403 embedded in cable jacket 405. Age sensors 403 may be a conductive composite of cable jacket or insulated conductor 407 polymers co-extruded in jacket 405. In other embodiments, conductive composites utilized in age sensors 403 may be made of other polymers designed to degrade in a manner similar to insulated conductors 407 or jacket 405.

A composite condition or age sensing instrument such as ohmmeter 409 may comprise a probe 411 having terminals 413 spaced to provide a resistivity measurement of age sensors 403 when contacted with age sensor 403. Terminals 413 comprise a predetermined spacing 415 to provide a resistivity reading of age sensors 403 which comprise a predetermined width 417 and predetermined thickness 419.

FIG. 5 is an alternative embodiment 501 of the cable of Fig 4 having a continuous condition/age sensor strip 503. Sensor strip 503 comprises a predetermined width and thickness similar to age sensors 403 of FIG. 4.

FIG. 6 is an embodiment of another method of monitoring age sensors 603 of cable 601 by utilizing radio frequency identification (RFID) tag assemblies 605. Tag assemblies 605 comprise age sensors 605 made from a conductive composite connected to an RFID chip 607. RFID chip 607 may comprise an antenna 607 for active or passive communication with a reader 609. A plurality of tag assemblies 605 may disposed in cable 601, for example by attaching assemblies 605 to tape 611 and wrapping tape 611 around insulated conductors 613. Tape 611 may comprise an adhesive surface 615 for retaining tag assemblies 605. In still other embodiments, a RFID tag assembly 605 may be connected to sensor loop311 of cable 301 of FIG. 3 and embedded in cable 301.

FIG. 7 shows the method of FIG. 4 applied to other extruded or cast polymer products 701 such as extruded or cast polymer siding, extruded or cast polymer pipe or tube, extruded, cast or laid-up composite structures such as aircraft structural parts and boat

hulls. Age/condition sensors 703 are made from conductive composites as discussed in previous examples, and may be co-extruded, cast, or they may be applied as conductive hot-melt or adhesive composites. Continuous age sensor strips such as strip503 of FIG. 5 may be substituted for age sensors 703.

In the preferred embodiments, age sensor conductive composites utilize the base polymer of the structure they are monitoring, such as the insulation polymer for wire and cable age sensors, or PVC for house siding. In some embodiments, the age sensor composite may be "designed" to age at the same, or in some cases faster than the base polymer by altering the filler content, adding or deleting anti-oxidants to the age sensor, or "pre-aging" the age sensor by accelerated aging techniques to match aging performance with the polymeric structure being monitored. These techniques may also be used to alter the response of the age sensor to more nearly follow natural aging of the polymer.

Although the description above contains many specifications, these should not be construed as limiting the scope of the invention but merely providing illustrations of some of the presently preferred embodiments of this invention. Thus the scope of the invention should be determined by the appended claims and their legal equivalents, rather than by the examples given.

Claims

I Claim:

1. A method of determining degradation of a polymer, the method comprising the steps of:
adding conductive particles to the polymer to form a conductive matrix comprising a preselected weight percent of conductive particles;
making an electrical connection with the conductive matrix and measuring an electrical property of the conductive matrix; and
equating the measured electrical property of the conductive matrix with the electrical property of a previously-degraded sample of the conductive matrix to determine the degradation of the polymer.

2. The method of claim 1 wherein the measured electrical property is electrical resistivity.

3. The method of claim 1 wherein the measured electrical property is electrical conductivity.

4. The method of claim 1 wherein the degradation of the polymer is mechanical degradation of the polymer.

5. The method of claim 4 wherein the mechanical property comprises a durometer of the polymer.

6. The method of claim 4 wherein the mechanical property comprises an elongation property of the polymer.

7. The method of claim 4 wherein the mechanical property comprises a hardness of the polymer.

8. The method of claim 4 wherein the mechanical property comprises a tensile strength of the polymer.

9. The method of claim 4 wherein the mechanical property comprises a toughness of the polymer.

10. The method of claim 1 wherein the degradation of the polymer is a chemical degradation.

11. The method of claim 10 wherein the chemical degradation comprises a measure of oxidation of the polymer.

12. The method of claim 10 wherein the chemical degradation comprises a measure of a remaining amount of anti-oxidant added to the polymer.

13. The method of claim 1 wherein the previously degraded sample was degraded by an accelerated aging means.

14. The method of claim 13 wherein the accelerated aging means comprises aging in an environment elevated in temperature as compared to the normal operating temperature of the polymer.

15. The method of claim 13 wherein the accelerated aging means comprises aging in an elevated radiation environment.

16. The method of claim 13 wherein the accelerated aging means comprises aging in an elevated humidity environment.

13. A degradation sensor for a polymeric structure, the sensor comprising:

a first quantity of conductive particles dispersed in a first portion of the polymeric structure to define a conductive matrix portion, the first portion comprising less than a total polymer in the structure; and

a means for communicating an electrical measurement of the conductive matrix to an electrical measurement apparatus.

14. The degradation sensor of claim 13 wherein the means for communicating an electrical measurement of the conductive matrix comprises a portion of the conductive matrix disposed on an outside surface of the polymeric structure.

15. The degradation sensor of claim 13 wherein the means for communicating an electrical measurement of the conductive matrix comprises a metallic conductor communicating with the conductive matrix.

16. The degradation sensor of claim 13 wherein the means for communicating an electrical measurement of the conductive matrix comprises a electromagnetic emitter.

17. The degradation sensor of claim 16 wherein the electromagnetic emitter is a radio frequency identification tag.

18. The degradation sensor of claim 13 wherein the conductive matrix defines a filament disposed in the polymeric structure.

19. The degradation sensor of claim 13 wherein the conductive matrix defines an extruded strip in the polymeric structure.

20. The degradation sensor of claim 13 wherein the conductive matrix defines a plurality of portions of conductive matrix, said plurality of portions of conductive matrix being separated from each other.

21. A polymeric structure comprising:

a degradation sensor for a polymeric structure, the sensor comprising:
a first quantity of conductive particles dispersed in a first portion of the polymeric structure to define a conductive matrix portion, the first portion comprising less than a total polymer in the structure; and
a means for communicating an electrical measurement of the conductive matrix to an electrical measurement apparatus.

22. The polymeric structure of claim 21 wherein the polymeric structure is an electrical wire.

23. The polymeric structure of claim 21 wherein the polymeric structure is an electrical cable.

24. The polymeric structure of claim 21 wherein the polymeric structure is a pipe.

25. The polymeric structure of claim 21 wherein the polymeric structure is a building siding.

26. The polymeric structure of claim 21 wherein the polymeric structure is an aircraft composite structure.

27. The polymeric structure of claim 21 wherein the polymeric structure is a boat hull.

Abstract of the Disclosure

An electrical condition monitoring method utilizes measurement of electrical resistivity of a conductive matrix disposed in a polymeric structure. The conductive matrix comprises a base polymer and a conductive filler . The method comprises a means for communicating the resistivity to a measuring instrument and a means to correlate resistivity of the conductive matrix of the polymeric structure with resistivity of an accelerated-aged conductive matrix.

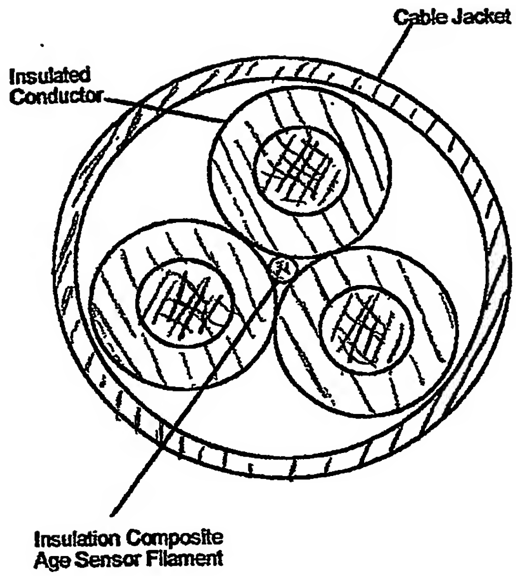
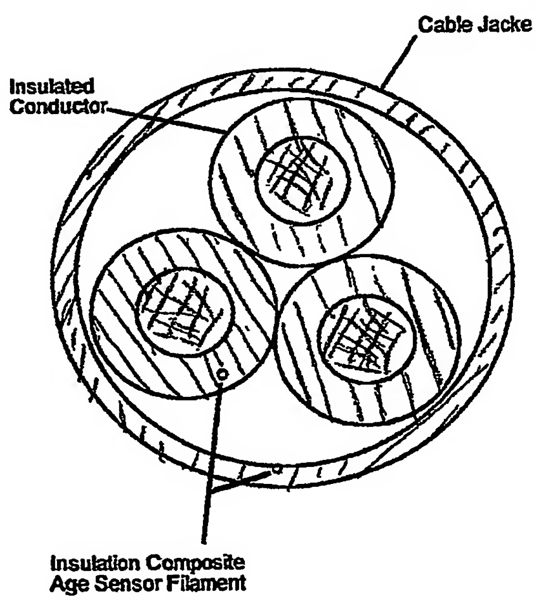

Cable Jacket
Insulated
Conductor
Insulation Composite
Age Sensor Filament

FIG. 1


Cable Jacke
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Age Sensor Filament

FIG. 2

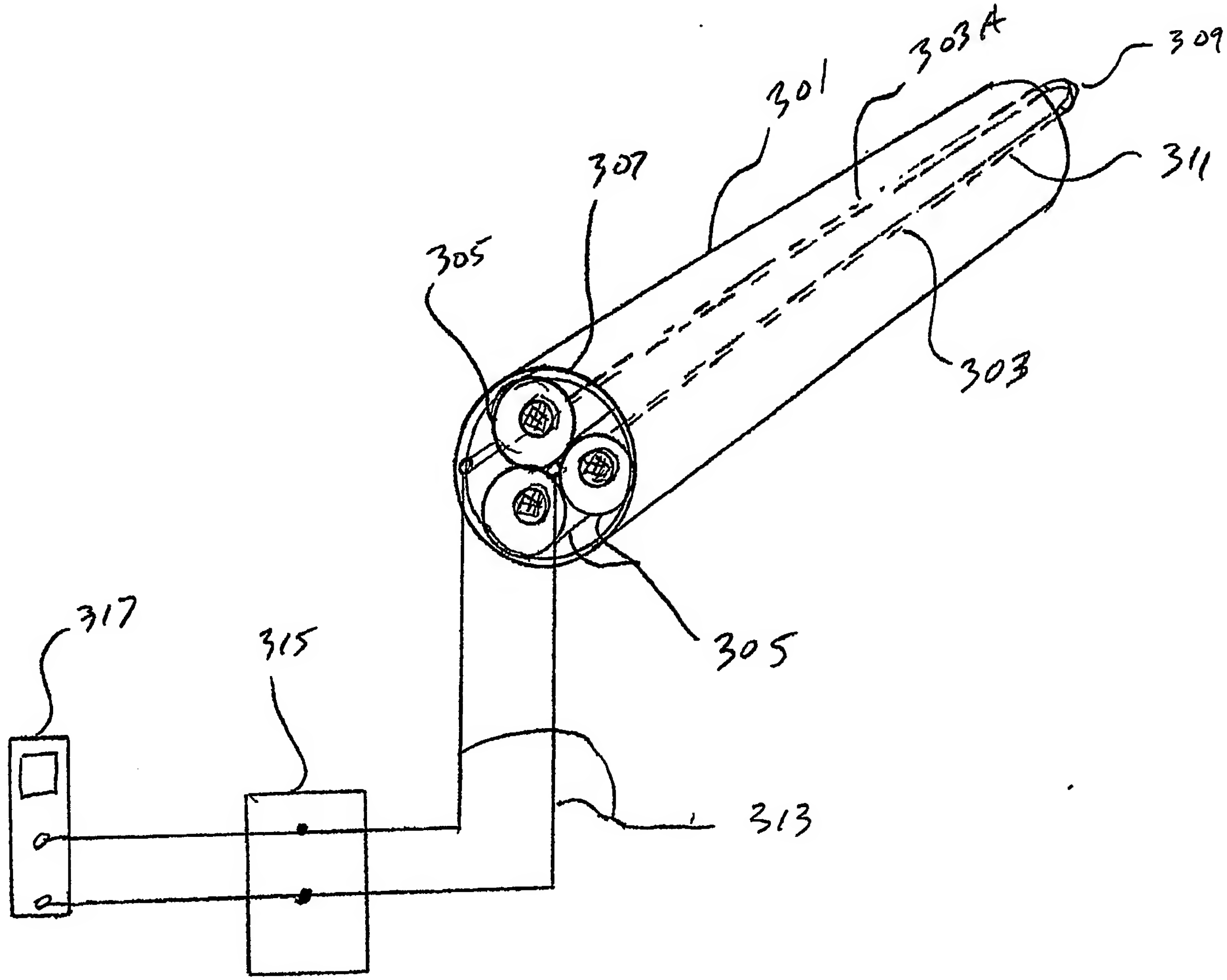
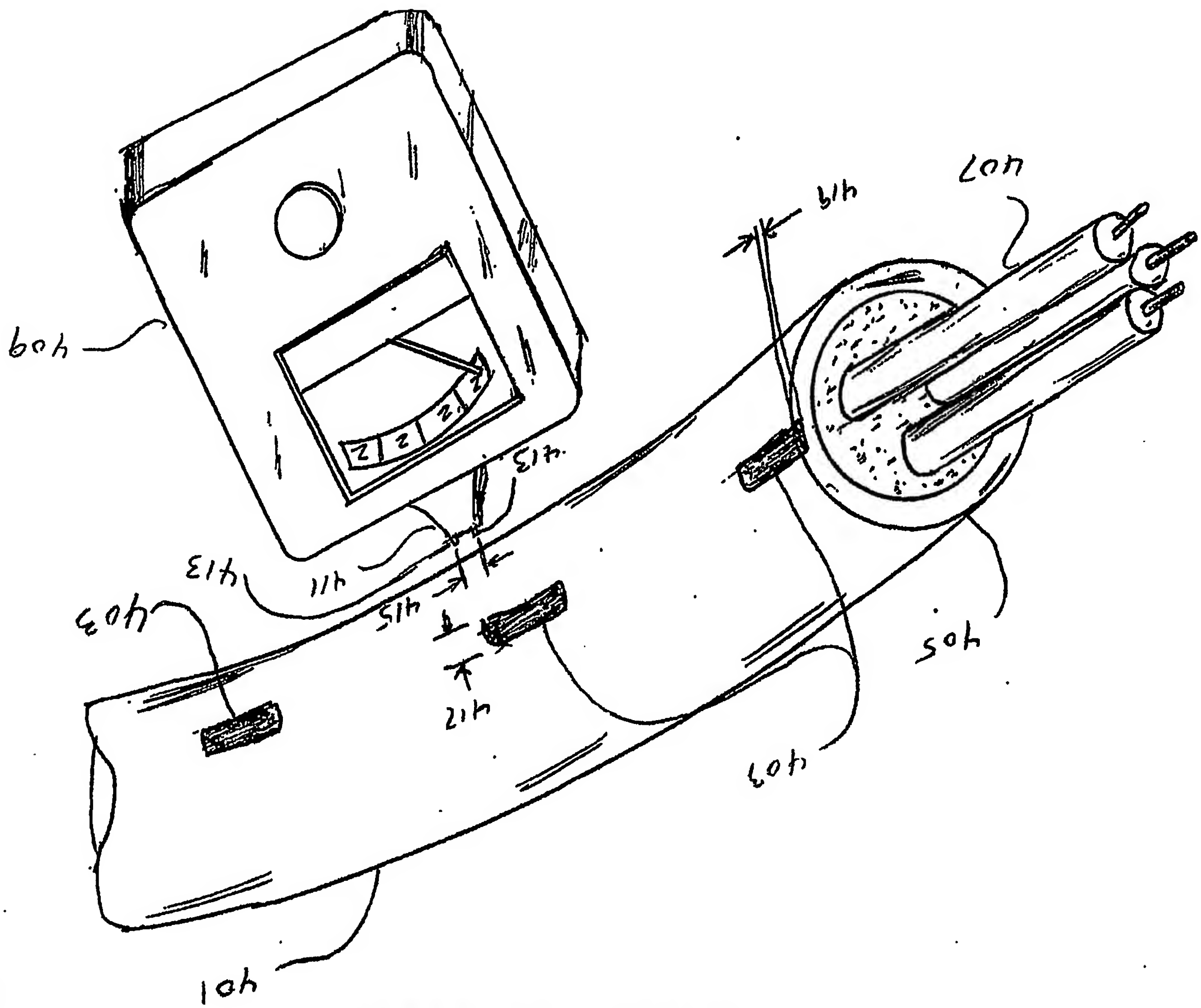


FIG. 3

FIG. 4



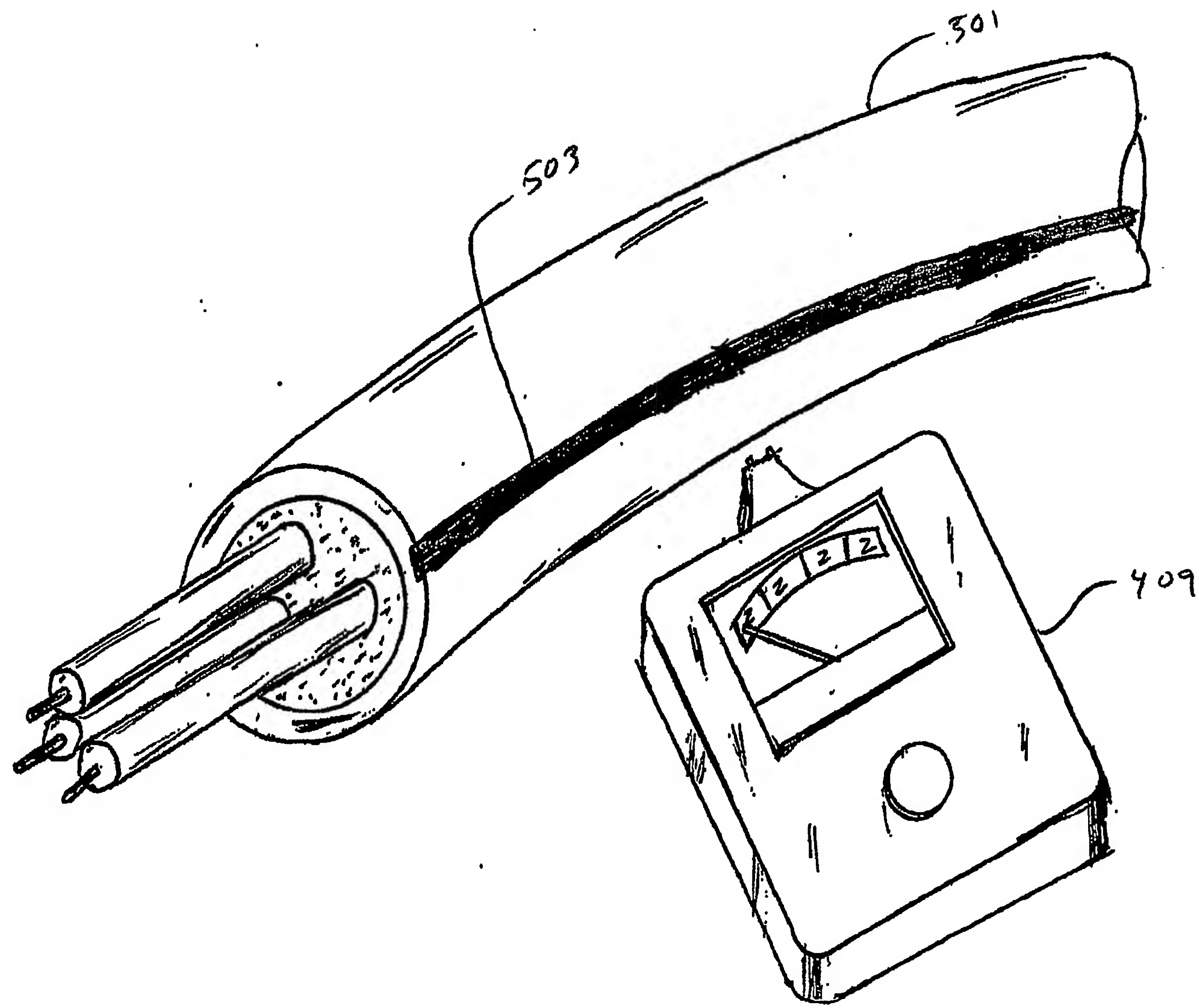


FIG. 5

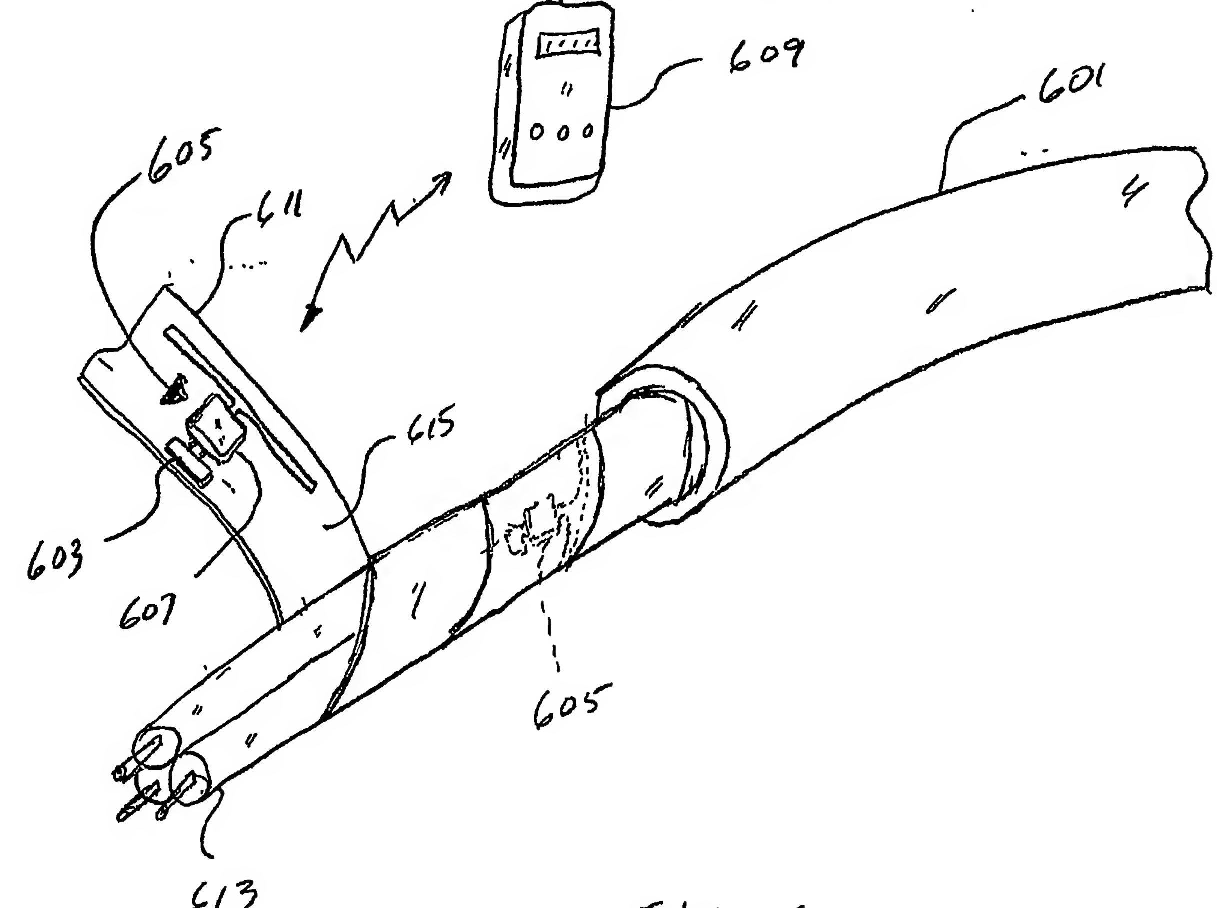


FIG. 6

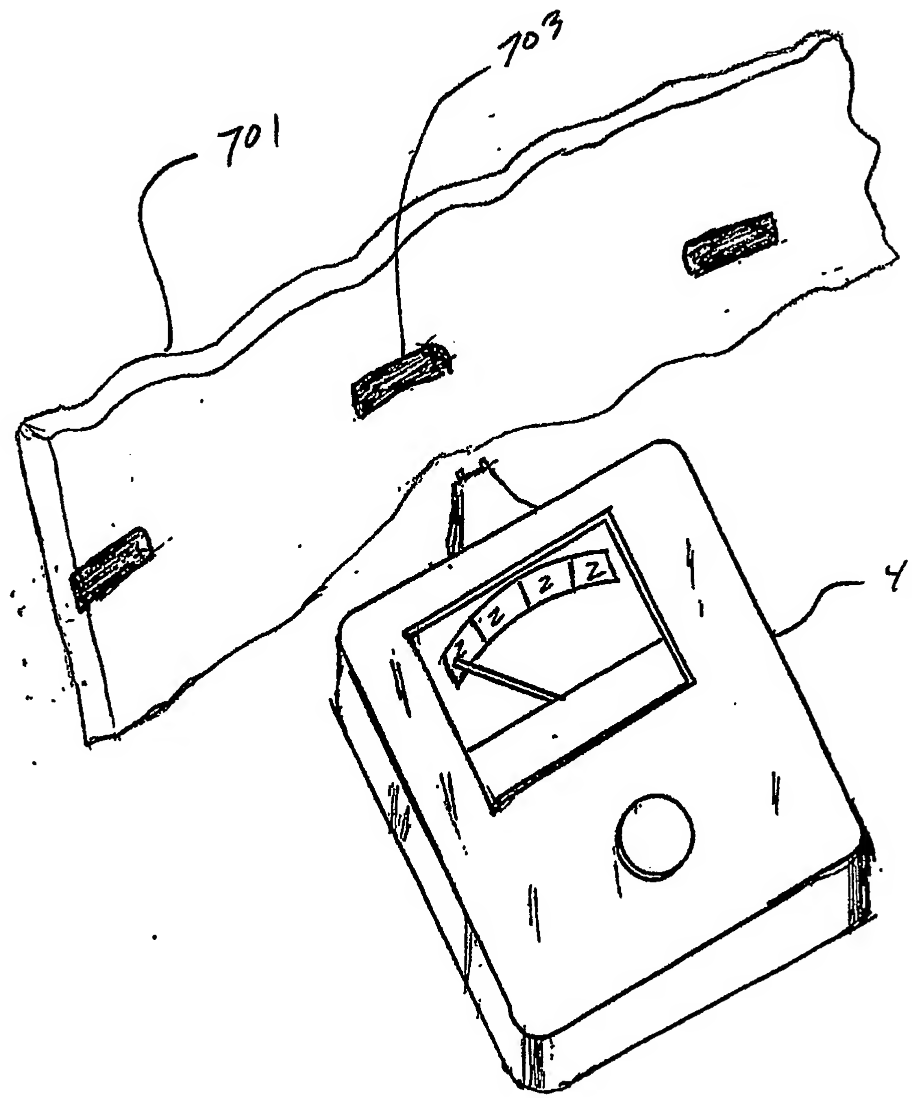


FIG. 7

"An Electrical Condition Monitoring Approach for Wire and Cable"

1.0 Significance and Background Information and Technical Approach

1.1 Project Objectives and Significance of the Research

The primary objective of this Phase 1 SBIR/STTR project is to determine the feasibility of utilizing electrically conductive polymer composites of insulation materials to provide an improved cable condition monitoring (CCM) method for Generation IV nuclear power plants.

A second objective of this project is to provide a cable condition monitoring method which can be measured in the field without removing wire and cable insulation samples and can be carried out with simple equipment and minimal operator training.

This proposal directly addresses the DOE Phase 1 SBIR/STTR solicitation under topic 14, "Advanced Technologies for Nuclear Energy", subtopic a. "New Technology for Improved Nuclear Energy Reactors". Specifically, this proposal addresses the need for assessing plant and equipment performance and monitoring aging. The proposed research is new and unrelated to the current Phase 2 project "The Development of ShortWatch, a Novel Overtemperature and Mechanical Damage Sensing Technology for Wires or Cables", currently in the second year of a two-year funded study by BPW, Inc.

The proposed CCM method utilizes inert conductive particles compounded with candidate insulation materials to provide a simple electrical measurement correlating to age-related degradation of mechanical properties and allowing determination of the remaining life of the insulation material. The conductive particles provide a large decrease in electrical resistivity corresponding to the tiny decreases in the volume (shrinkage) of the insulation material that occur during the natural aging process of the insulation. The shrinkage is due to cross-linking of the polymer chains during aging, providing a denser packing of the polymer chains.

The electrical cable condition monitoring proposed under this solicitation, if found feasible, will provide a vast improvement over current mechanical and chemical condition monitoring techniques. *It will provide a distributed, in-situ method that is independent of access considerations and destructive testing, increasing safety by monitoring areas otherwise impractical or impossible. It will reduce the cost of Generation IV cable condition monitoring by reducing sample-retrieval time and testing costs associated with conventional mechanical and chemical condition monitoring.*

1.2. Background

Wire and cable are critical to the safe and reliable operation of nuclear power plants. The polymeric materials used in wire and cable insulation and jacketing (and other polymers) degrade with age, especially in severe environmental conditions. The safe operation of existing and future plants requires monitoring of the insulation materials in order to anticipate degradation before performance of the wire and cable is adversely affected.

Wire and cable aging is primarily a mechanical failure mechanism. As the insulation ages, it becomes embrittled and eventually fails mechanically by cracking and exposing bare conductors. The industry has spent considerable time and effort to develop condition monitoring methods which monitor installed wire and cable and ensure that the materials have not degraded

xcessively. These methods are also used to predict safe operating lifetime of wire and cable insulation materials for anticipated environmental conditions. Presently, cable condition monitoring (CCM) methods are categorized as mechanical methods, chemical methods and electrical methods.

Elongation-at-break (EAB) has traditionally been one of the most common and well-documented CCM methods. This mechanical method measures the elongation of a sample of insulation material just prior to break and is normally expressed as a ratio of the break length divided by the original length of the sample. Since elongation measured in the test is analogous to elongation occurring when bending wire and cable, the results can be easily correlated to actual wire and cable insulation condition. Arrhenius methods described by Gillen et al. (Reference 8) are normally used to predict material lifetime at a target ambient temperature from acceleration-aged data.

A serious disadvantage of the EAB method is that a relatively large sample portion is required to perform the test. This makes the test essentially destructive since the cable is rendered inoperative when the sample is removed. Even if a cable is sacrificed in order to run a test, some portions of the cable may be difficult or nearly impossible to access for sample removal, as would be the case if the area of interest is within a cable bundle, wire tray, or internal to a penetration. The equipment needed for measurement is relatively expensive and requires specialized skills.

Indenter modulus test is a relatively new mechanical test that utilizes a machine to press a small anvil at constant velocity against the outer surface of the cable or insulated conductor while measuring the force exerted on the anvil. The indenter modulus is defined as the slope of the force-position curve. A major advantage of the indenter modulus test is that the test itself is non-destructive. However, the test is of limited use on conductor insulation since access to a sufficient length of individual conductors is often restricted. Also, the test is not practical on cable within cable bundles or trays, or in other confined spaces.

Oxidation Induction Time (OIT) is a chemical condition monitoring method that utilizes small (8-10 mg) samples removed from cable insulation materials. The method utilizes a differential scanning calorimeter (DSC) to provide an indication of the rapid oxidation of the sample when anti-oxidants, normally present in the insulation material, are exhausted. Short induction times indicate exhaustion of the anti-oxidant and anticipate rapid degradation of the material. Sample collection requires access to the cable which limits testable portions of the cable. Measurement requires expensive laboratory equipment and specialized training.

Electrical condition monitoring methods include insulation resistance, high potential tests, tan-delta tests, and ionized gas medium tests. These tests are essentially "go no-go" tests since no well-established methods reliably predict insulation lifetime based on the results. Several of these tests require high electrical potentials to be connected to cables, requiring removal of connected equipment and loads in order for the tests to be performed.

[redacted].3 Technical Approach and Benefits of the Research

The methodology of the proposed condition monitoring method utilizes the electrical resistivity of a conductive composite formed from a candidate insulation material as a highly sensitive measurement of a mechanical property (volume shrinkage). Volume shrinkage, in turn, will be correlated as a mechanical indicator of insulation material aging. The method, if found feasible, will eliminate disadvantages of current methods and provide a condition monitoring method which improves safety and reduces condition monitoring costs for new generation plants.

The incorporation of inert conductive particles into the insulation to form a conductive composite provides several significant advantages for cable condition monitoring:

(1) A small change in volume of the conductive composite results in a large change in electrical resistivity. A few percent change in volume fraction of the insulation material provides a potential of 3 – 5 orders of magnitude change in the resistivity of the composite. This high measurement sensitivity provides an opportunity to detect and monitor small aging effects which current cable condition monitoring methods are insensitive to; and

(2) Measurement of the electrical resistivity is a simple measurement requiring no special equipment, expertise or removal from service.

The conductive composite sensor may be distributed within electrical cables as a separate filament, or it could be co-extruded as a filament in wire and cable insulation or jackets. The filament ends would be series connected or grounded to allow measurement at one end of the cable. An example of an age-sensing filament positioned in a multi-conductor cable is shown in figure 1 below.

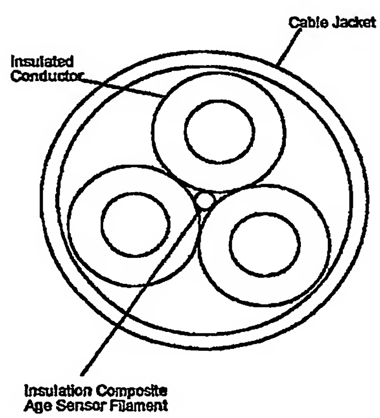


Figure 1: Composite filament in multi-conductor cable

Figure 2 below shows an example of a composite co-extruded in the insulation of a conductor and co-extruded in the jacket of the cable.

REF (A)

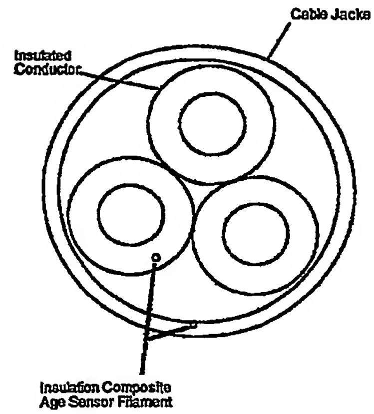


Figure 2: Co-extruded composite filaments in multi-conductor cable

The potential impacts of this method, if feasible, are significant and would provide the following benefits:

(1) Cable condition monitoring would be done in the field with simple electrical measurement equipment such as a digital multi-meter;
(2) Access is required only to the cable terminations;
(3) The cable remains fully operable during monitoring;
(4) Multiplexing would monitor condition of multiple wire and cables "in-situ"; and
(5) Datalogging would provide continuous histories of cable condition.

If the end-of-life response of this method is non-linear, as indicated in preliminary testing, accelerated aged portions of the cable could be detected and potentially located by standing wave ratio (SWR) or time domain reflectometry (TDR) technologies.

2.0 <u>Phase 1 Project</u>

2.1 Technical Objectives

The primary technical objective of this phase 1 project is to determine the feasibility of utilizing conductive composites as a condition monitoring approach and to identify the additional work needed to provide a fully capable method during a phase 2 project. The feasibility of the approach will be demonstrated by:

1. Showing a correlation of volumetric shrinkage of a candidate insulation material with age; and
2. Showing a correlation of electrical resistivity of a conductive composite of the insulation material with the measured volumetric shrinkage (and age).

Correlations of these phenomenon will demonstrate that a simple electrical measurement (resistivity of the insulation composite) equates to a predictable age of the insulation material.

This phase 1 project will also identify a Phase 2 research and development plan which would fully develop a cable condition monitoring program utilizing this approach. For example, the phase 1 project will identify additional candidate insulation materials, conductive fillers, test methodology and sensitivity factors which might affect the results of the method.

2.2 Overview of the Phase 1 Work Plan

In order to support the objectives of the Phase 1project, a research and development plan will be implemented to:

(1) Provide a better understanding of volumetric shrinkage of polymers and, specifically, polymers used in nuclear wire and cable insulations as a function of age. A model of volumetric shrinkage as a function of age is critical because the electrical measurements made possible by conductive composites of these materials will be the "indicator" of volumetric shrinkage, not a direct measurement of aging itself.

Very limited prior work has been found in volumetric shrinkage of insulation polymers as a function of age, probably due to the fact that the shrinkage is small (only a few percent at end-of-life) making the measurements in the field difficult and, until now, offering no apparent advantages over current methods of cable condition monitoring.

Significant related work has been done in the area of insulation *density* measurements as a condition monitoring approach. For example, Gillen et al. have done extensive investigations of wire and cable insulation and jacket material density as a condition monitoring method. The densification observed during aging is described as being due to several mechanisms including replacement of light hydrogen atoms with much heavier oxygen atoms during oxidation. A second mechanism disclosed by Gillen et al. (Ref. 10, page 7,8) is a volumetric shrinkage due to cross-linking of the polymer chains causing a tightening of the polymer network.

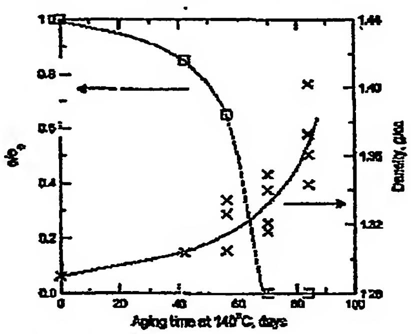


Fig. 10. Density and elongation results versus aging time for the XLPO insulation aged at 140°C.

Figure 3: Density and elongation vs. age time (Gillen et al.)

It is this volumetric shrinkage mechanism during aging on which this portion of the project will focus. A literature search will be carried out by BPW, Inc., and Dr. C. P. Wong of the School of Materials Science and Engineering. In addition, consultation with Electric Power Research Institute (EPRI) and the Organic Materials Aging and Reliability Department of the Sandia National Laboratories will be requested during this phase of the research. Volume measurements of aged and unaged samples of cross-linked LDPE insulation composite materials produced during the ShortWatch SBIR, as well as other candidate insulation materials may be conducted during this phase to gain a clearer understanding of the shrinkage mechanism.

(2) Research candidate conductive polymer composites based on current and proposed insulation materials used in nuclear power plants. Selection of candidate conductive polymer composites

Our study comprises three parts: selection of a candidate insulation "base" material, selection of an inert conductive "filler" and designing a "recipe" and extruding the candidate insulation composite. Due to the time limitations of the Phase 1 project, one or two composites will be selected and evaluated for testing. More extensive composite selections will be made during the Phase 2 project.

Selection of the insulation "base" material will focus first on wire and cable materials that are candidates for Generation IV nuclear power plants. EPRI, DOE and its laboratories, nuclear wire and cable manufacturers, engineering firms and NSSS suppliers will be consulted as part of the candidate insulation material selection process.

Dr. Wong of the School of Material Science and Engineering will provide the lead research in selection of the conductive filler and develop a "recipe" for the candidate insulation composite. Consideration will be given to ensuring chemical inertness with the candidate insulation base material, low "intrinsic" resistivity, high transition response, sensitivity to non-age-related factors, cost and environmental considerations. The research and development group of Rockbestos Surprenant Cable Corp. will be consulted during this phase of the research for processing and manufacturability issues.

(3) <u>Design test plan to provide volume shrinkage and resistivity data as a function of age in order to correlate a CCM method</u>. In order to provide data for a preliminary model for insulation composite aging, the test plan must provide highly accurate volume shrinkage and electrical resistivity data as a function of age. The test plan will incorporate additional mechanical and/or chemical cable condition monitoring tests such as elongation-at-break (EAB) or density to act as a control and provide additional data with which to correlate the results of the tests. The test plan will address the method(s) of accelerated aging (thermal, radiation, humidity), test temperatures, radiation dose rates, aging time, diffusion-limited-oxidation (DLO) considerations, sensitivity to non-age-related factors, configuration and type of samples, test equipment type and procedures, measurement equipment and controls and test procedures.

One of the biggest challenges of developing the test plan will be the determination of the aging method and conditions used in the accelerated aging tests. Work by others (Gillen et al., Ref. 5) points out limitations in the use of Arrhenius methodology used to project expected life of a polymer at temperatures significantly lower than those at which the accelerated aging was carried out. In general, this work shows problematic areas including determination of effective activation energies, and diffusion-limited oxidation (DLO) effects. Generally, the lower the temperature selected for thermal aging, the less problematic these issues become. However, low oven temperatures for accelerated thermal aging require long test durations (effectively approaching natural aging in the extreme case).

The volume shrinkage mechanisms of the proposed methodology are highly sensitive to the amount of crystallinity present in polymers. The crystalline portions of the polymer are more tightly-packed and therefore, comprise less volume than an equivalent mass of non-crystalline (amorphous) regions. Any environmental factors which change the crystallinity of the candidate polymer will affect the measured volume of the insulation polymer. Accelerated thermal aging of cross-linked LDPE insulation composite at 160C (significantly above the transition

temperature of 106C) demonstrated a marked increase in resistivity. This increase in resistivity (due to volume increase of the insulation fraction) of the composite is believed due to cross-linking the polymer in the melted state. Cross-linking of the polymer in the melted state immobilizes the chains sufficiently to prevent re-crystallization when the polymer is cooled. This analysis is supported by measurements made on the fully aged samples, indicating a total loss of crystallinity at 883 hours when aged at high temperatures relative to the transition temperature.

The implications of the sensitivity to the crystallinity of polymers of this process may limit its use to low-crystallinity polymers if the selected thermal aging temperature is above the transition temperature. This "de-crystallization" phenomenon is not expected to be an issue in low-crystallinity material such as EPR's, nor for radiation or thermal aging at temperatures below the transition temperature. In fact, regardless of the condition monitoring method being used, thermal aging below the transition temperature is a good practice because it is detrimental to introduce micro-structural changes in the material that would otherwise not occur during natural aging, regardless of the test method used. The extremely high sensitivity of the composite insulation material to volume changes may allow the natural aging results for relatively short time periods to be correlated with accelerated age testing.

BPW, Inc. and Georgia Tech will develop the test plan with input from EPRI and Rockbestos. Consultation will be requested from the Organic Materials Aging and Reliability Department of the Sandia National Laboratories, as well as input from members of the Cable and Condition Monitoring Group of EPRI.

(4) Run aging tests BPW, Inc. and Georgia Tech will perform aging tests in accordance with the test plan.

(5) Evaluate the data and develop a preliminary CCM model. Test data will be collected and evaluated in order to determine the feasibility of electrical resistivity measurements to provide a valid cable condition monitoring method. The data will provide a basis for establishing correlation of measured resistivity changes and sample volume shrinkage as a function of aging. Data collected on mechanical or chemical methods will be checked to see if established CCM results correlate to the resistivity changes of this method. Arrhenius methodology will form the basis for this analysis. The extremely high sensitivity of the process may allow evaluation of very small aging effects as would occur from short durations of natural aging. Such changes could be checked for correlation with predicted age effects from accelerated aging. The full development of a CCM model utilizing conductive composites will be done under a Phase 2 project if approved.

2.3 Phase 1 Task Plan

2.3.1. Research volumetric aging mechanisms of polymers

Aging effects on polymers will be researched specifically to identify the fundamental mechanisms of volumetric changes during the aging process of polymers. Literature searches and consultation will be conducted by BPW and Georgia Tech, to determine prior work in both theoretical and experimental areas. This work will be used to: (1) better understand the

volumetric mechanisms of aging of polymers in general and insulation materials in particular; (2) verify that results of previous age testing on ShortWatch composite sensors agrees with volumetric changes predicted by the literature; and (3) provide a basis for designing the test plan in the later tasks of the project. Consultation with Sandia National Laboratory will be requested since considerable work on density (as opposed to volumetric) changes of insulation materials with aging has been done at the lab. Four weeks have been allotted for this task.

2.3.2. Research candidate insulation materials

Wire and cable materials will be researched to identify candidate polymers that will be used as the base material for the composites used in the aging trials. Special emphasis will be made on polymer compounds used, or anticipated to be used, in wire and cable insulation and jacketing in the nuclear power industry. Research will focus on mechanical property effects of aging on candidate materials from thermally and radiation-accelerated aging, as well as natural aging. The new EPRI Cable Condition Monitoring (CCM) Database will provide an extensive resource for insulation material aging data. BPW, Inc. will provide lead activities for this task with assistance from Georgia Tech. Four weeks have been allotted for this task.

2.3.3. Research conductive fillers

The School of Materials Science and Engineering at Georgia Tech will provide lead research activities for conductive particle fillers for use with candidate base materials identified in Task 2. This research will key on compatible fillers which optimize electrical detection of volumetric changes in the base polymer. Rockbestos will provide consultation services on conductive fillers based on their practical experience in compounding conductive matrixes. BPW will provide coordination with Rockbestos and DOE consultants during this task. Four weeks have been allotted for this task.

2.3.4. Select candidate composite(s) (Milestone)

BPW, Inc. will coordinate research activities with Georgia Tech and consult with EPRI, Rockbestos and DOE laboratory(s) in the selection of one or more conductive polymer composites for use in the age trials of the test plan. Georgia Tech will research composite "recipes" of the candidate base polymer, conductive fillers, anti-oxidants and other components that optimize electrical resistivity changes with volumetric changes in the base polymer. Rockbestos will provide consultation on composite mixing and extrusion experience. Selection criteria will include potential use of (or compatibility with) nuclear industry insulation materials as the base polymer, projected sensitivity of the composite in detecting volumetric changes based on aging, projected sensitivity to non-age-related effects such as environmental conditions and composite material strain, manufacturability and cost. At least one composite will be selected for use in the test plan. Additional composites may be selected, if necessary, to meet the goals of the project. Two weeks have been allotted for this task.

2.3.5. Develop test plan for selected composite(s) (Milestone)

BPW will coordinate development of a test plan to (1) measure volumetric and electrical resistivity changes in the selected composite as a function of accelerated age time, and (2) measure established cable conditioning quantities such as elongation-at-break with accelerated age as a control. Other mechanical and chemical properties, including anti-oxidant levels during aging, will be considered for use in correlating aging mechanisms involved. Georgia Tech, EPRI

and Rockbestos will be consulted and provide input to the test plan. Two weeks have been allotted for this task.

2.3.6. Extrude sample specimens
Rockbestos will compound and extrude specimens of the selected composite(s) for accelerated aging trials, as determined in the test plan. Three weeks have been allotted for this task.

2.3.7. Assemble materials and test specimens
BPW and Georgia Tech will assemble materials and test specimens for aging as determined in the test plan. This may include custom test specimen packaging or preparation as specified in the test plan. Four weeks have been allotted for this task.

2.3.8. Assemble and configure test equipment
BPW and Georgia Tech will assemble and configure test equipment for aging specimens as determined in the test plan. This will include assembling, calibrating and testing laboratory ovens for thermally accelerated. Electrical equipment for measurement of resistivity and mechanical test equipment for measurement of sample volume, elongation-to-break, etc. will be assembled, calibrated and tested. Four weeks have been allotted for this task.

2.3.9. Run aging tests
BPW will coordinate aging tests run at the sites as determined by the test plan. Six weeks have been allotted for this task. The selection of this time period is based on a balance of using the lowest possible test temperatures for thermal aging consistent with time and cost considerations.

2.3.10. Evaluate and correlate test data (Milestone)
BPW will coordinate evaluation of data provided by the aging tests to determine correlation of electrical resistivity and volumetric changes in the candidate composite(s) with accelerated aging of the specimens. The results of these correlations will be checked by comparison with established cable condition monitoring data such as elongation-at-break run as control specimens in the trial. Correlation of predicted quantities will be compared with natural aging to the extent possible. Georgia Tech will perform the evaluation in consultation with EPRI and DOE field laboratories. Two weeks have been allotted for this task.

2.3.11. Write final report (Milestone)
BPW will write the final report for the project based on the evaluation results of the test plan. Two weeks have been allotted for this task.

2.4 Performance Schedule and Milestones
The project schedule is found in Appendix A. Detailed task descriptions are shown in section 2.3 of the previous section. Major project milestones are as follows:

Milestone	Schedule Task No.
Select candidate composite(s)	4
Develop Test Plan	5
Evaluate and Correlate Teat Data	10
Write Final Report	11

2.5 Related Research and R&D

The fundamental basis for this study arose from observations during accelerated aging of conductive composite samples of a fault-sensing sensor filament for an unrelated DOE SBIR entitled "The Development of ShortWatch, a Novel Overtemperature and Mechanical Damage Sensing Technology for Wires or Cables." The conductive composite sensor filament formed the overtemperature-sensing component of a multi-conductor cable system and comprised an electron-beam cross-linked LDPE base polymer and a carbon-black conductive filler. The base polymer was an actual insulation material used in an environmentally-qualified wire and cable product (Rockbestos Surprenant Cable Corp. FireWall III™). The sensor filament detects overtemperature by a large increase in resistivity at the transition temperature resulting from an increase in the volume fraction of the polymer as the crystalline structure of the polymer "melts."

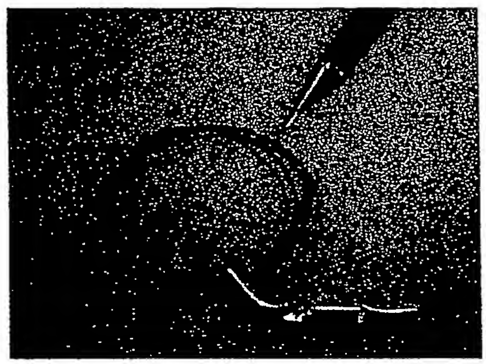


Figure 4: ShortWatch insulation composite filament

The aging tests showed approximately an order of magnitude increase in the resistivity after aging 286 hours at 160 °C, followed by approximately two orders of magnitude decrease in resistivity at the end of the test (883 hours). Durometer of the filament was measured and increased with oven age consistent with other known mechanical measurements.

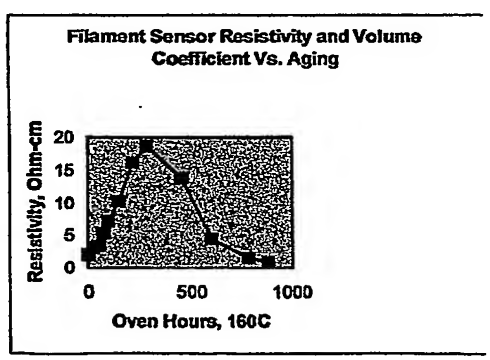


Figure 5: Resistivity-Age response of insulation composite

Resistivity of a conductive composite is primarily a function of the volume fraction of the base and filler components. Because the temperature of the aging was too low to suggest changes in

The carbon-black filler volume component, the results implied an initial volume increase of the LDPE component, followed by a decrease in the LDPE volume component. The decrease in resistivity during the later portion of the aging period is consistent with volume shrinkage of the insulation portion due to cross-linking as the polymer ages. However, the initial increase of resistivity was not consistent with the expected results.

Additional tests were run to determine the Resistivity-Temperature (switching) response of the sensor as a function of accelerated age. Switching performance dropped significantly as the oven age time increased.

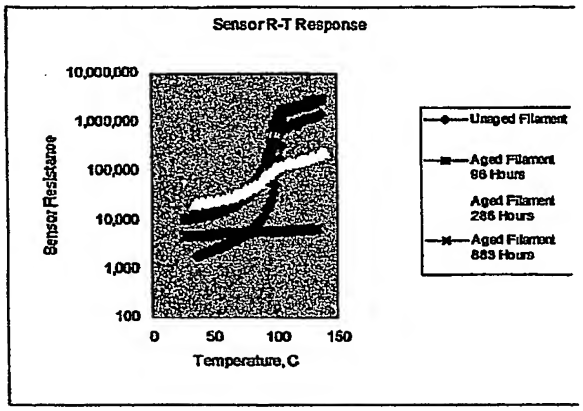


Figure 6: R-T response for unaged and aged samples

Both the high initial resistivity and the loss of switching response were consistent with loss of crystallinity due to the accelerated aging, so differential scanning calorimeter (DSC) tests on the aged and unaged samples were run at the School of Material Science and Engineering at Georgia Tech. The tests showed essentially a total loss of crystallinity with the 883 hour, oven-aged sample. Confirming tests were done on a commercial switching HDPE composite and similar results found.

Test results suggest that two phenomenon are taking place during accelerated aging at temperatures well above the transition temperature. One phenomenon is an increase in resistivity as a function of time due to cross-linking of the polymer chains, immobilizing them and preventing re-crystalization upon cooling. In other words, the microstructure is "locked" into an amorphous state and not allowed to re-crystallize when the composite is cooled. The second phenomenon is a reduction of resistivity due to the cross-linking of the amorphous regions. The first phenomenon is believed to predominate early in the accelerated age process at high temperatures relative to the transition temperature, and the second phenomenon occurs during any aging, but predominates upon the loss of most or all of the crystallinity of the material. The second phenomenon would be expected to accelerate upon depletion of anti-oxidants. FIG. 7 shows relative durometer readings of the filament as a function of oven aging. These results are

consistent with other mechanical condition monitoring measurements such as elongation-at-break.

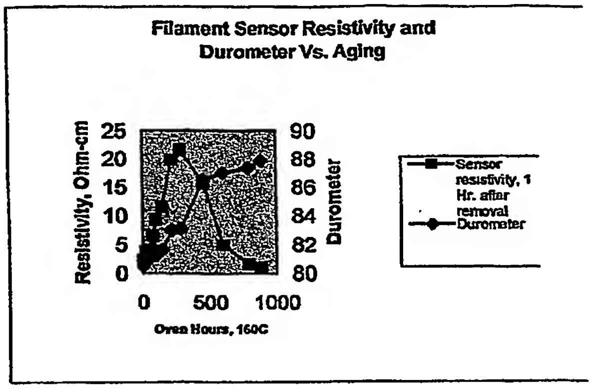


Figure 7: Resistivity and durometer vs. accelerated aging

Tests on natural-aged samples over a period of approxiimately nine months shows a decrease in resistivity with age, consistent with the cross-linking of the amorphous regions at temperatures below the transition temperature. The high initial loss of resistivity is believed due to "re-crystallization" following an annealing step.

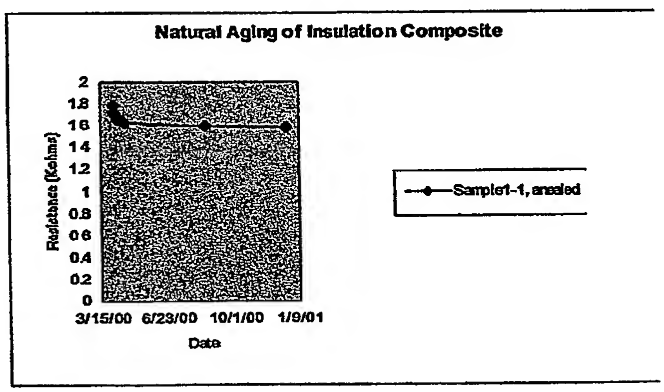


Figure 8: Resistivity vs. natural aging time

2.6 Potential Application of the Technology

FIG. 9 shows a curve of one possible response to an insulation material composite aged below the transition temperature. The curves anticipate an "induction time" effect after which rapid degradation follows due to consumption of anti-oxidants. The resistivity decreases due to volume shrinkage, and mechanical properties decrease consistent with known aging effects. The initial decrease in resistivity is due to "recrystallization" following a thermal processing step.

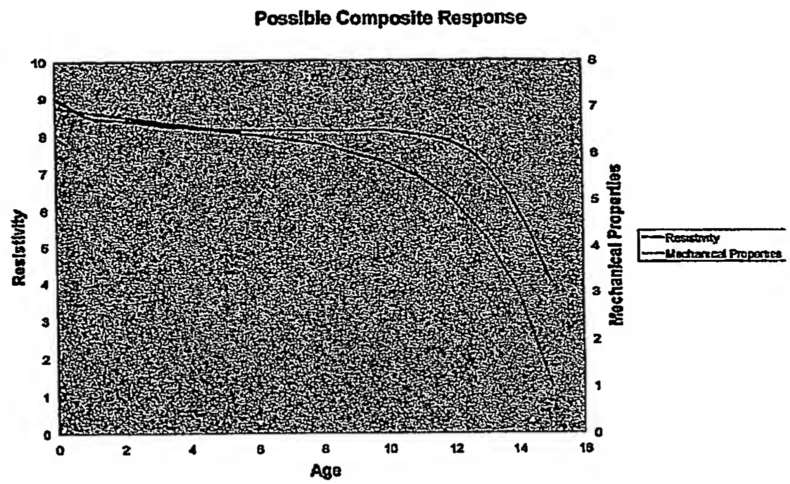


Figure 9: Projected resistivity and mechanical properties as a function of accelerated age

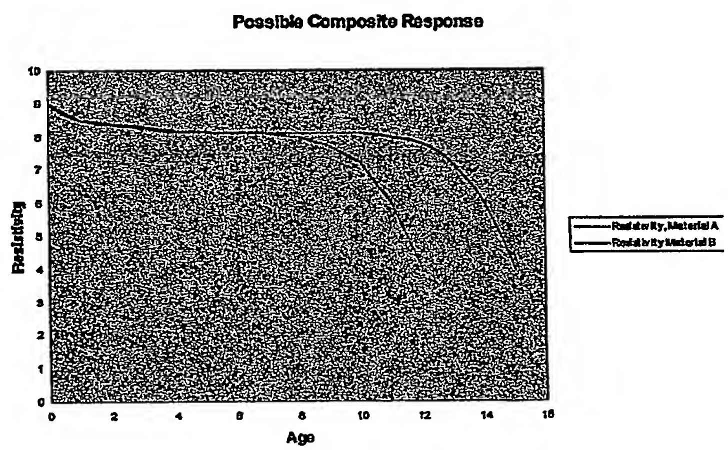


Figure 10: Projected resistivity vs. age for different filler loadings

FIG. 10 is an example of another possible application utilizing a "tracer" composite made from a low crystallinity base polymer and a conductive filler. Two possible anti-oxidant levels are shown as Material A and B. Such a "tracer" composite could be aged to provide an "integrated" age indicator by measuring the resistivity of the tracer composite as a function of accelerated age. Such a methodology would allow use of the "tracer" to indicate the accumulated age of any

material, including high crystallinity polymers and those aged at temperatures higher than the transition temperature of the target material.

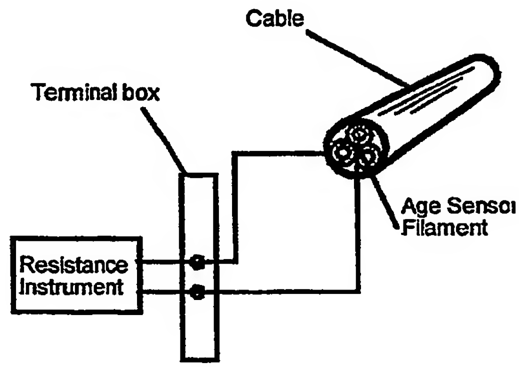


Figure 11 Monitoring of age sensor resistance

FIG. 11 shows a schematic diagram of an electrical connection for monitoring resistance of an age sensor filament distributed in a multi-conductor cable. The connections to the terminal box may be permanent or temporary connections. The resistance instrument may be a hand-held digital multi-meter, or an installed or portable datalogger. Multiple cables could be monitored by a multiplexing datalogger.

<u>**2.7 Importance of Proposed Project**</u>

This project, if shown feasible, will provide a significant improvement in cable condition monitoring for use in Generation IV nuclear power plants by:

- The ability to monitor the condition of representative wire and cable in currently inaccessible areas will improve plant safety and reliability over current condition monitoring methods;
- Elimination of the need to collect physical samples will improve personnel safety and plant reliability;
- The use of simple field instruments reduces equipment and labor costs associated with laboratory measurements; and
- The high sensitivity of the measurements will allow improved correlation with natural aging studies.

The condition monitoring method of this proposal may also be expanded to polymer applications in addition to wire and cable. For example, the methodology may have applications in condition monitoring of seals, diaphragms, shielding and other polymeric materials.

Proposal is currently pending.

.0 References

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An Electrical Condition Monitoring Approach For Wire and Cable

FY 2001 DOE SBIR Phase 1

DOE Grant No. DE-FG02-01ER83153

Awarded 8/27/01

REF. C

Agenda

- Basis, Background and Need
- Phase 1 Project Plan
- Trial Data and Analysis
- Applications and Manufacturability
- Future Work
- Commercialization Plan

REF. C

Basis

- DOE FY 2001 SBIR/STTR Solicitation
- "Advanced Technologies For Nuclear Energy" (Topic 14)
- "New Technologies for Improved Nuclear Energy Reactors" (Subtopic a)
- "Assess plant and equipment performance and monitor aging, by development of advanced diagnostic techniques for in-service and non-destructive examination"

REF. C

Background

- Current cable condition monitoring (CCM) methods:
  - Mechanical (EAB, indenter, density)
  - Chemical (OIT)
  - Electrical (insulation resistance)
  - Visual/tactile inspections

REF. C

Background

- Limitations of current (CCM) methods:
  - Access (cable trays, penetrations)
  - Destructive (EAB, density, OIT)
  - Expensive (labor/equipment)
  - High level of training
  - Repeatability of results

REF. C

Need

- Improved CCM method which:
    - Reduces access requirements for sampling
    - Non-destructive
    - Simple and repeatable
    - Lowers cost of condition monitoring

REF. C

Project Plan

- Concept: Utilize measurement of electrical resistivity of a conductive composite "tracer" to:
  - Equate mechanical properties of insulation material
  - Predict remaining lifetime

REF. C

Project Plan

- Theory: Resistivity of composite "tracer" changes in predictable ways as insulation (base polymer) ages.

Resistivity of the "tracer" is not a fundamental property of the base polymer, rather it is a sensitive tool for indirect measurement of mechanical properties.

REF. C

Project Plan

- Advantages of utilizing resistivity:
  - Low cost equipment (multimeter)
  - Simple (no extensive training required)
  - Repeatable results

REF. C

Project Plan

Task Plan

- Literature search
- Base polymer/filler selections
- Test plan
- Trials to obtain data
- Evaluation
- Future work (Phase 2, commercialization /implementation plan)

REF. C

Project Plan

Base Polymer/Filler Selections:

- Polymer candidates crystalline (XL-PE) and non-crystalline (EPR, silicone rubber)
- Fillers (carbon black, metallic)
- Selected EPR, carbon black filler, no anti-oxidants

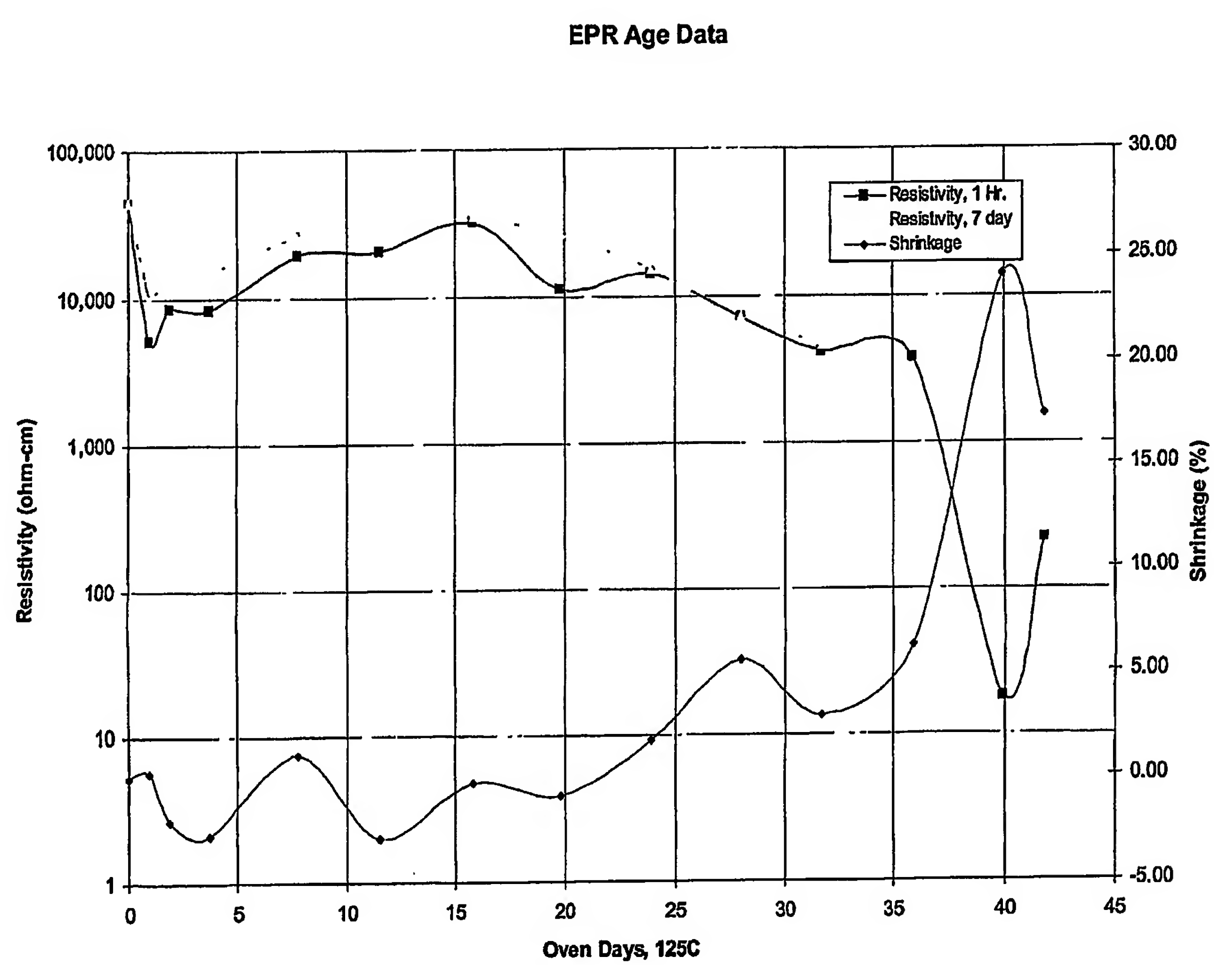
REF. C

Project Plan

Phase 1 Test Plan:

- Perform thermal/oxidative accelerated aging trial on EPR composite
- 125 C selected as non diffusion-limited oxidation (DLO) condition. No antioxidants.
- Measure resistivity, EAB, volume change mass, density
- Analyze data

Trial Data



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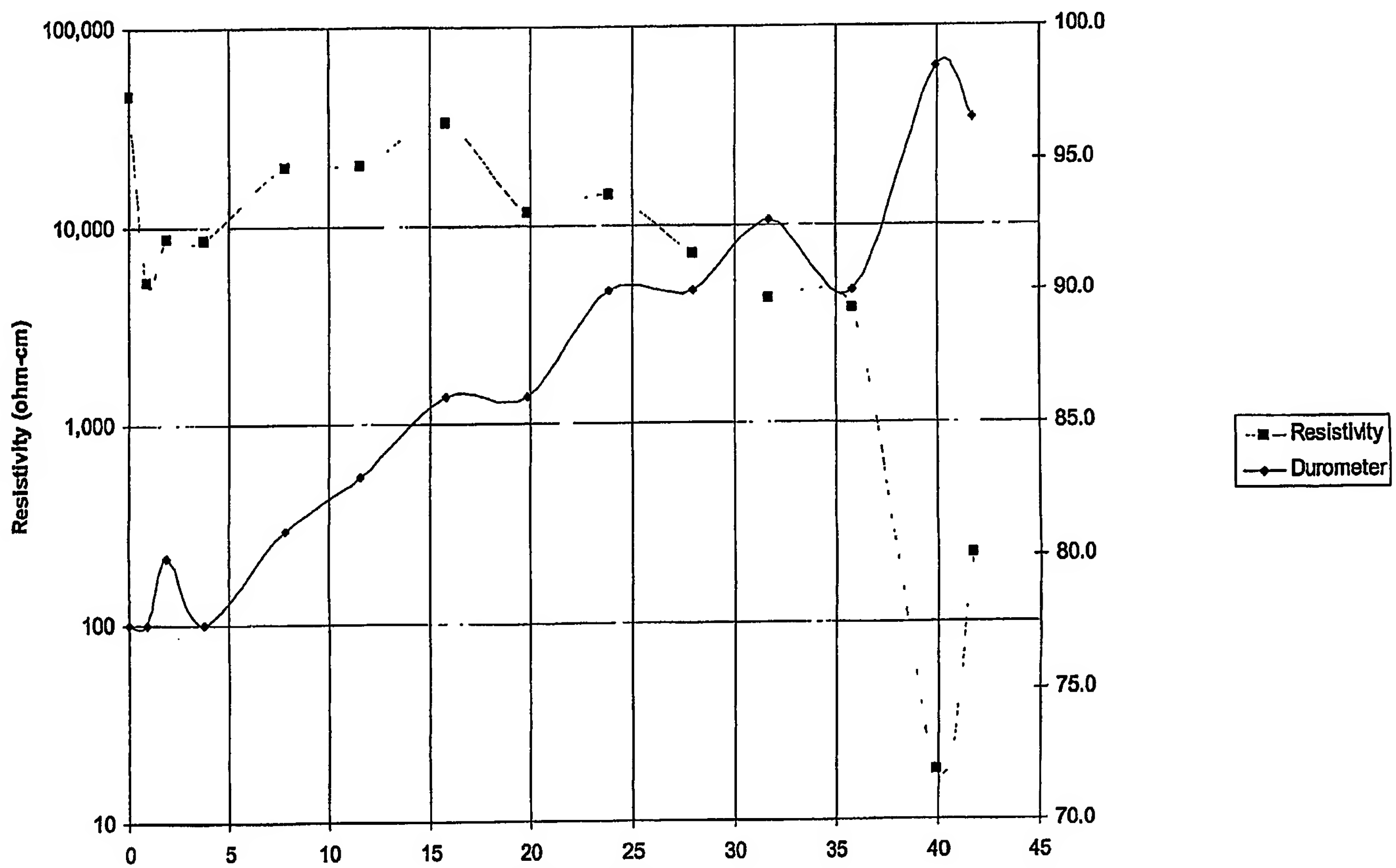
Trial Data

EPR Resistivity and Durometer vs Age



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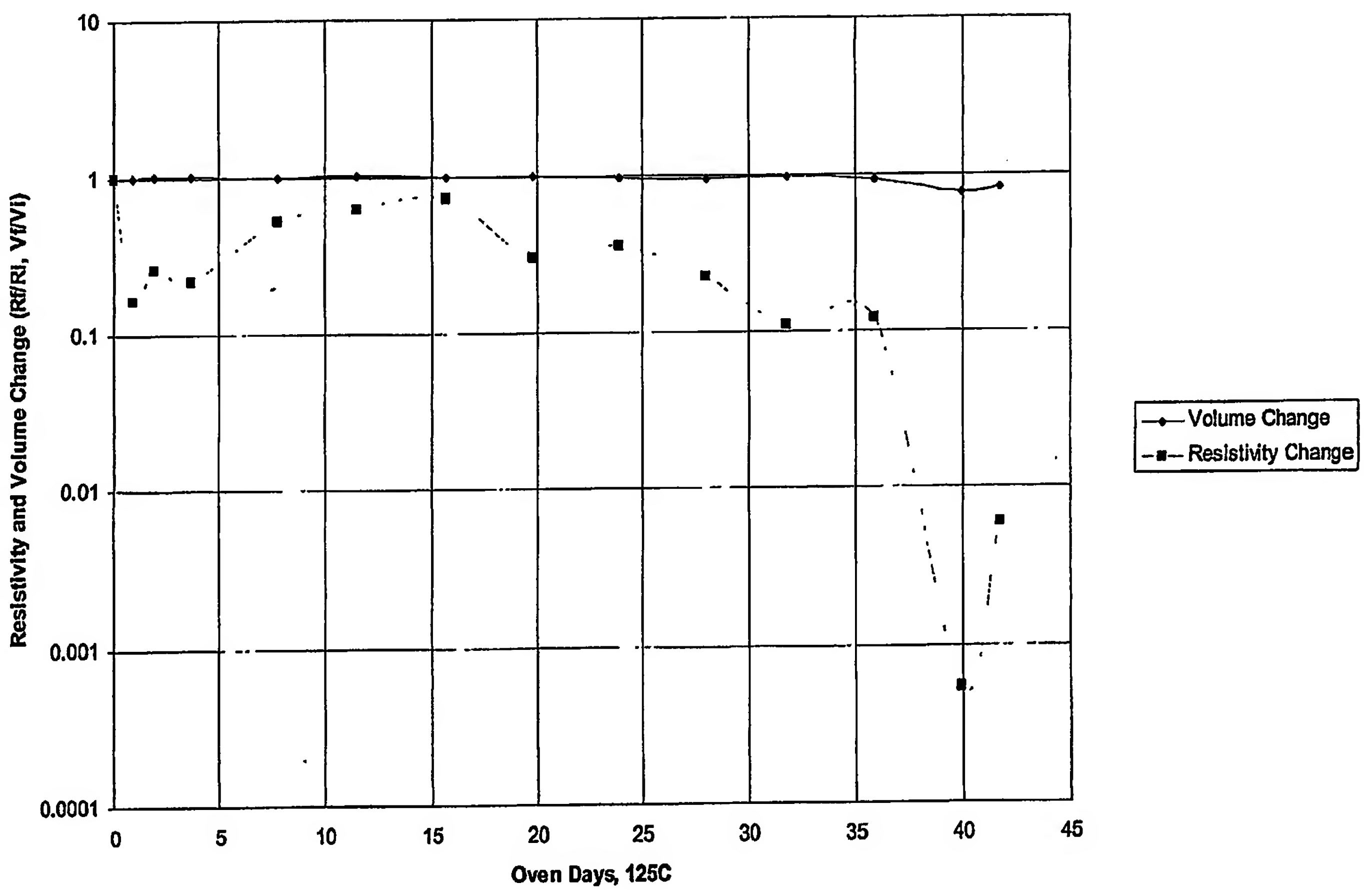
Trial Data

Resistivity Vs. Volume Sensitivity



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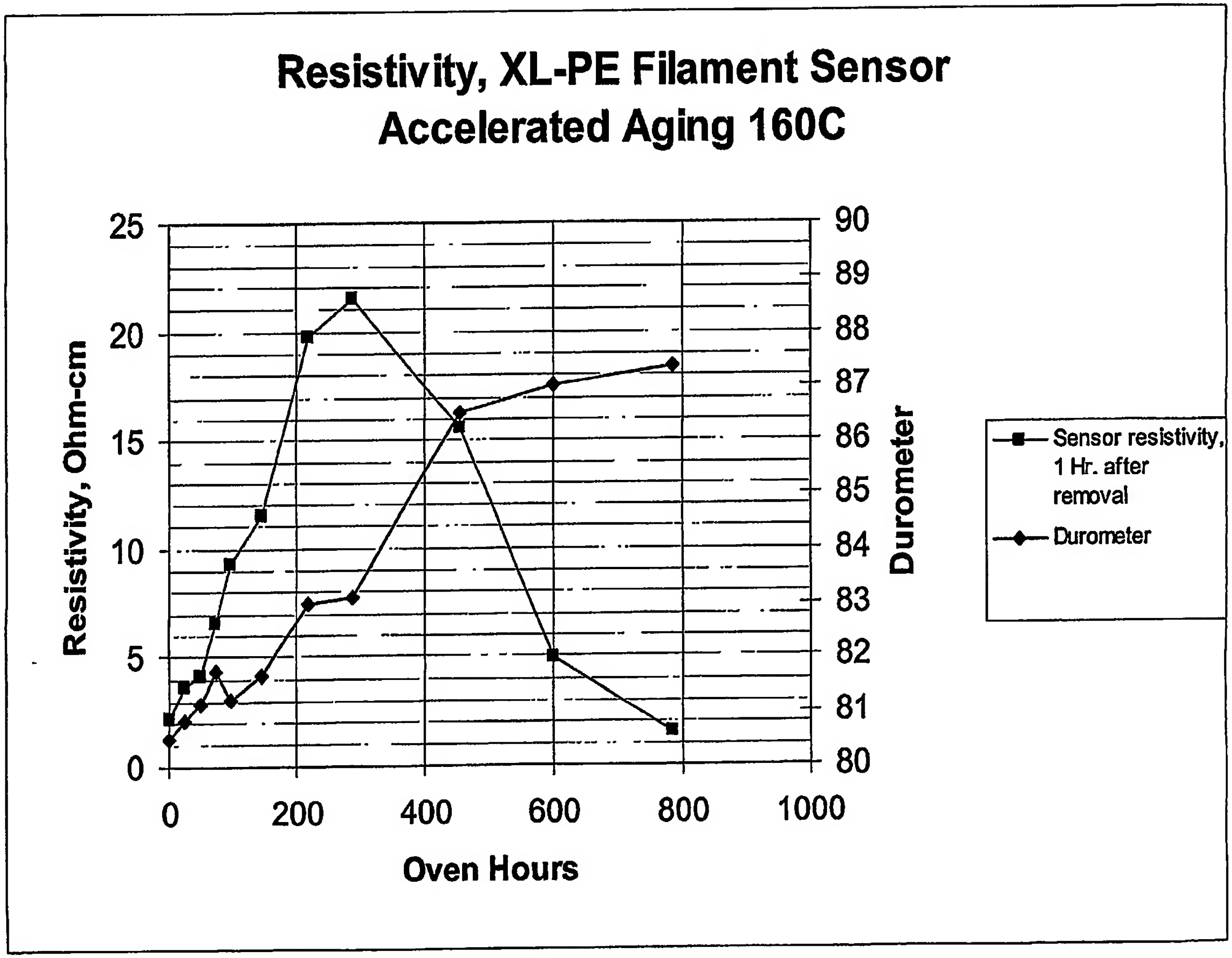

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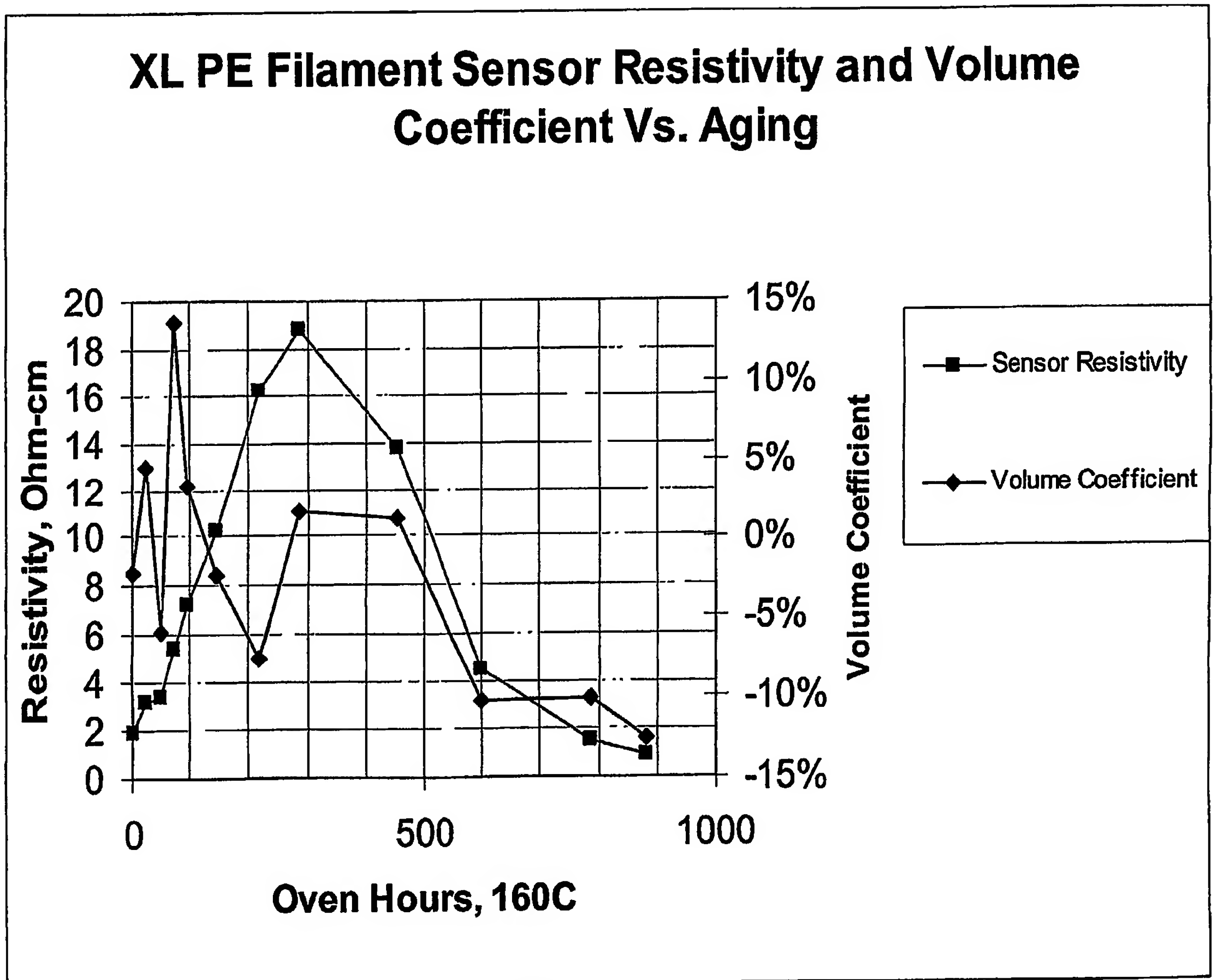

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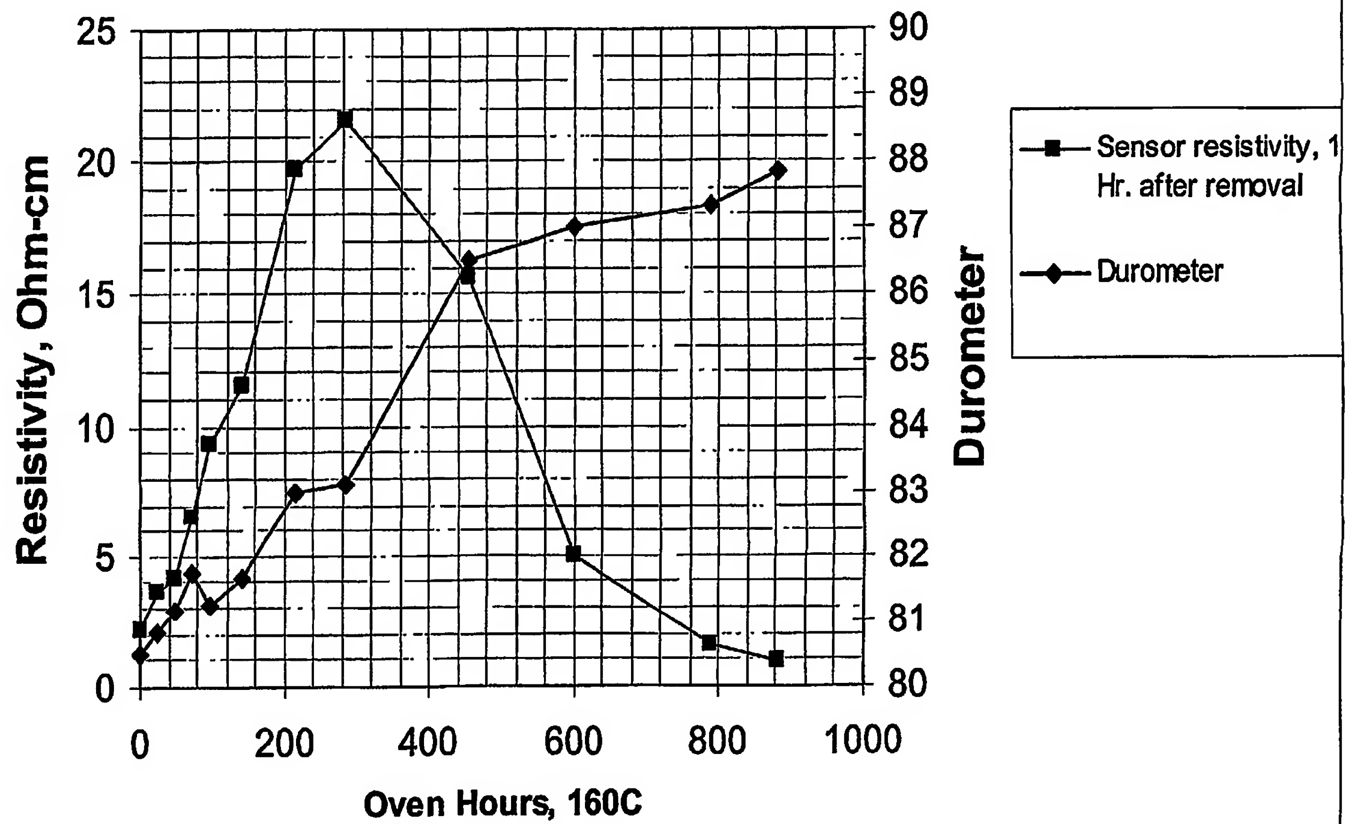
Trial Data

XL PE Filament Sensor Resistivity and Durometer Vs. Aging



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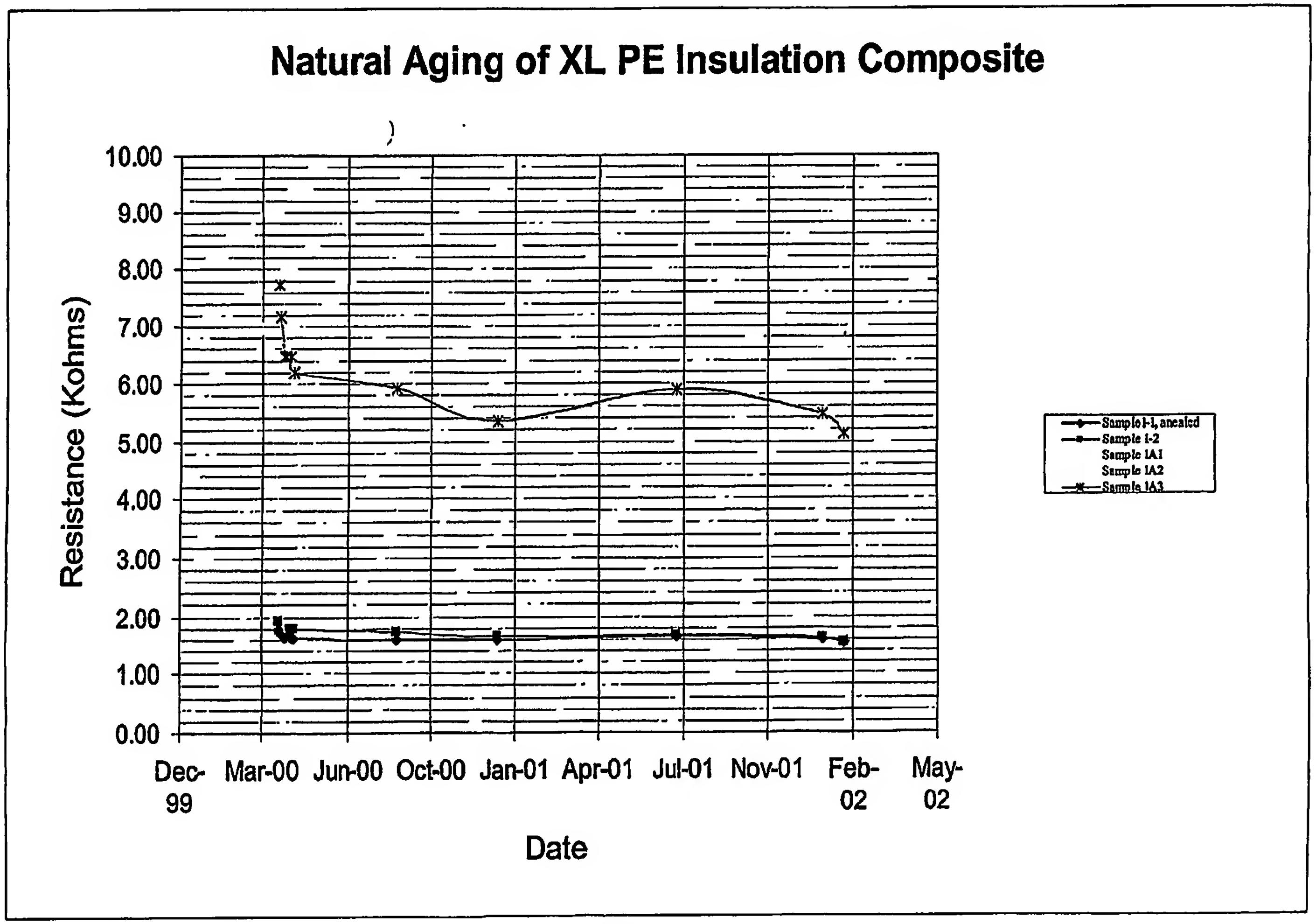

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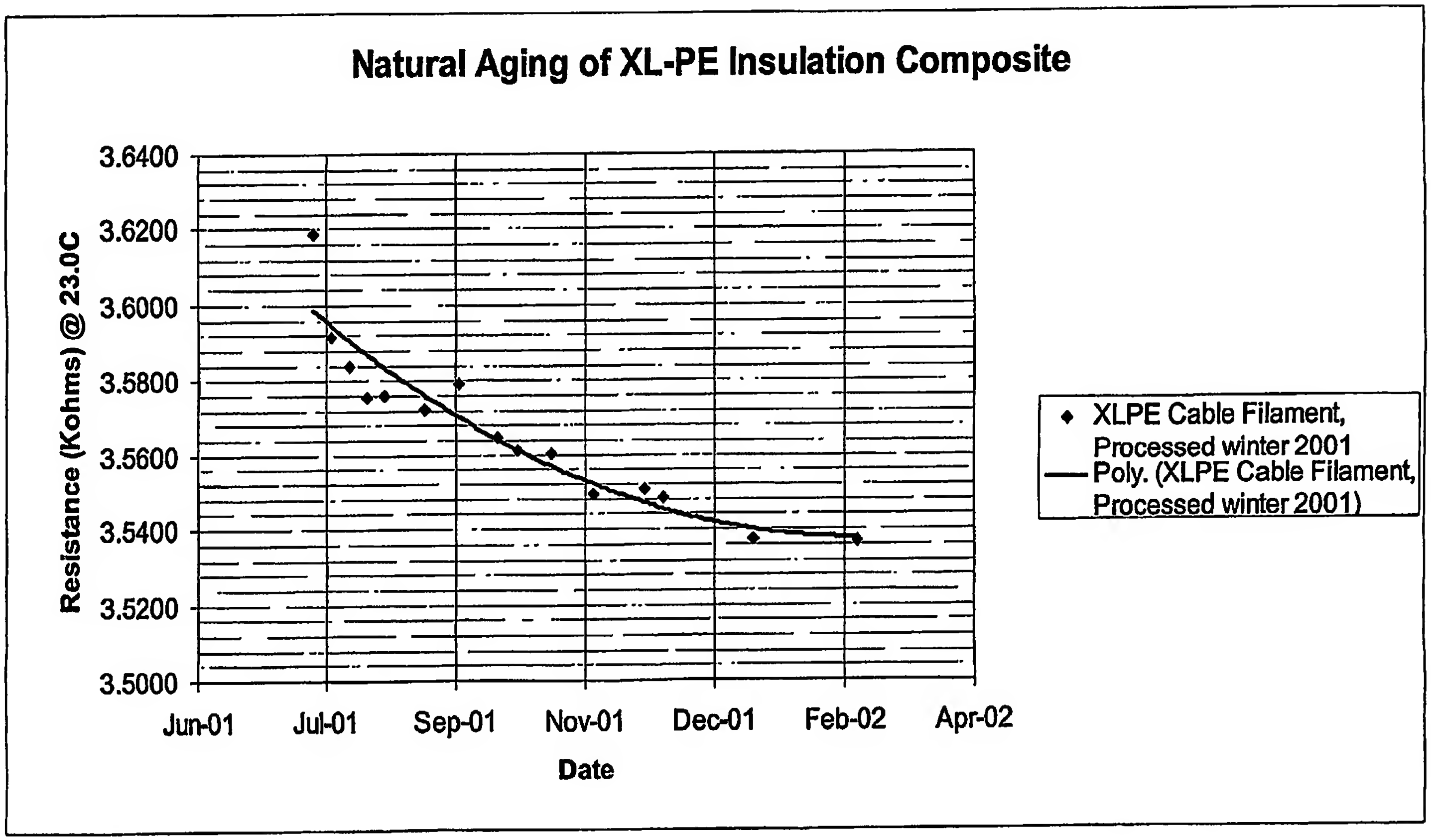

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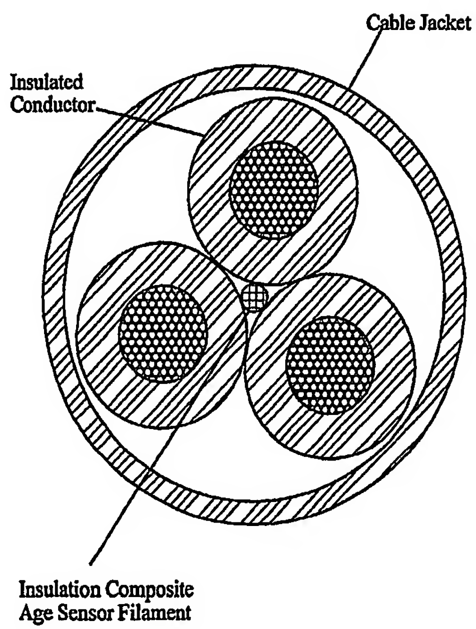
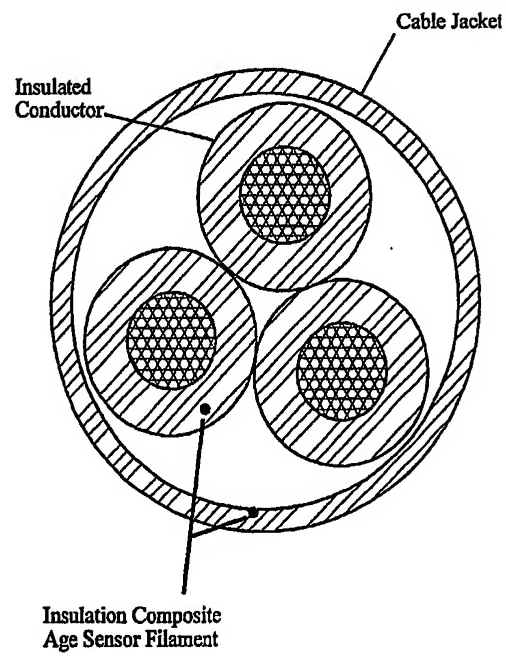
Applications

- Proposed Electrical CCM Cable Designs





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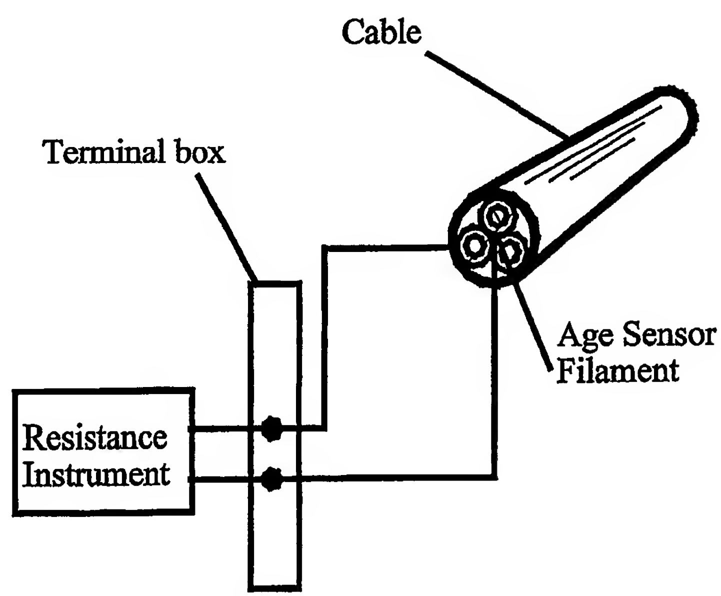
Applications

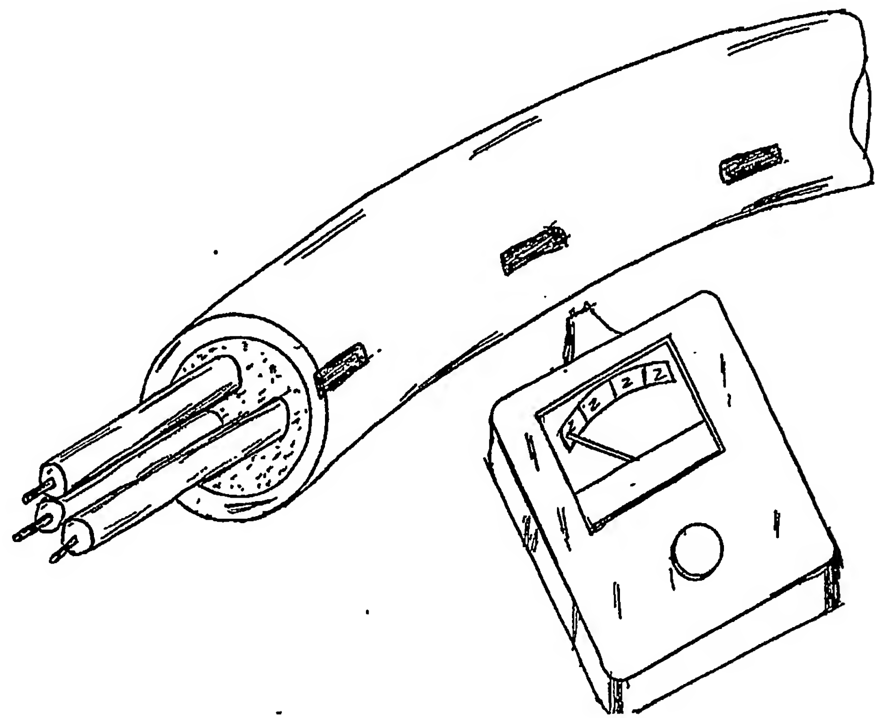
- Age Sensor Monitoring



REF. C

Applications

Field Sampling



REF. C

Analysis

- Implications if found feasible:
  - Remove CCM from laboratory to field/control room

REF. C

Future Work (Phase 2)

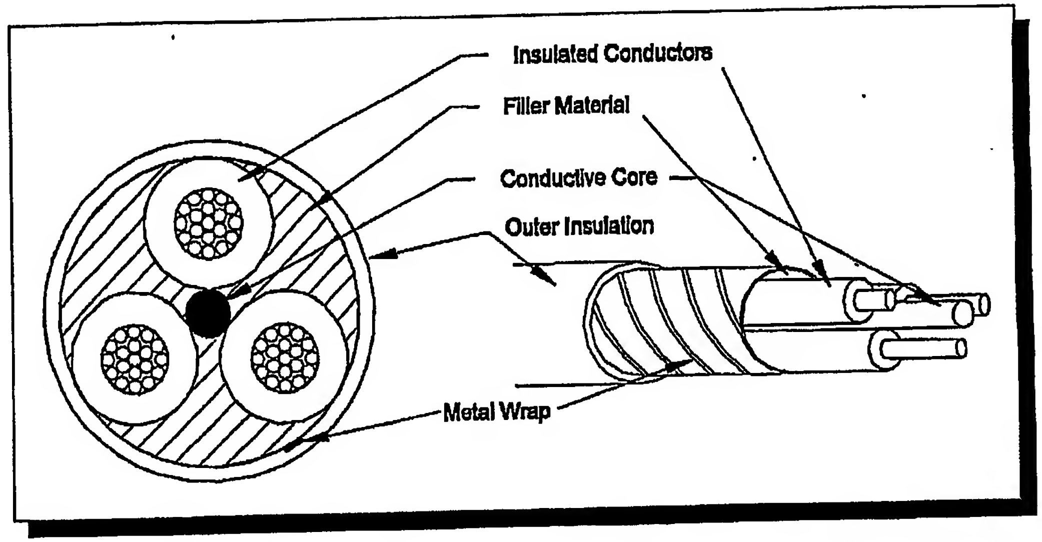
- Select candidate nuclear cable materials for trial
- Accelerated aging at multiple temperature/dose rate conditions
- Analytical methods to model remaining life
- Manufacture prototype cable for monitoring in field
- Demonstrate cable condition data retrieval (wired and RFID)

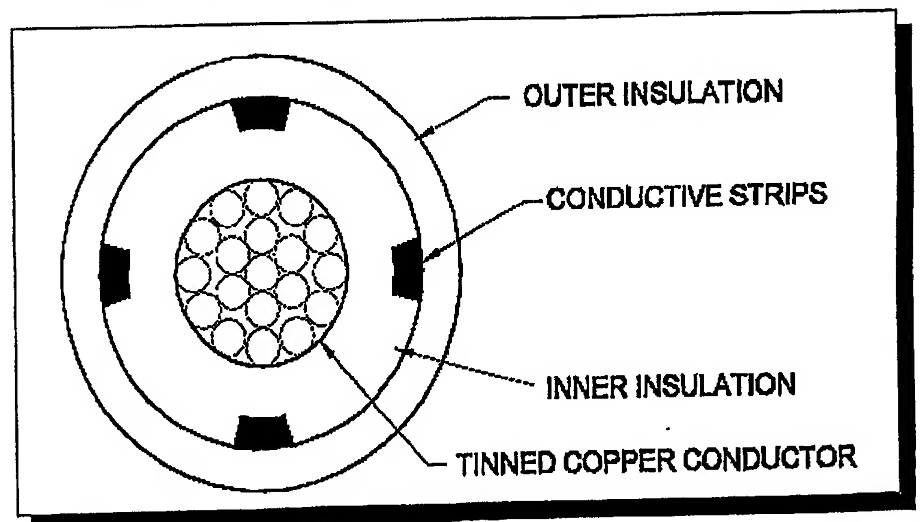
REF. C

20902E0" 4ST29E09

Prototype Wire Designs

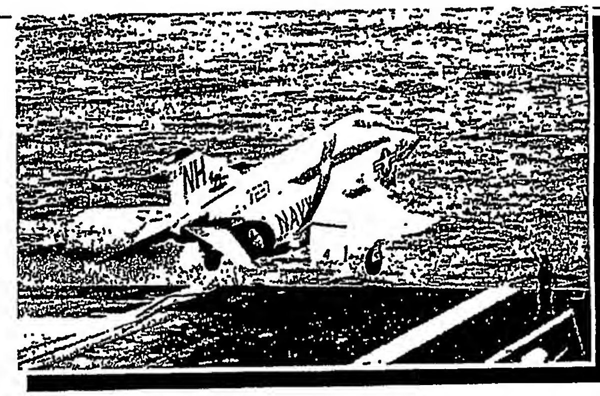
- Jacketed multi-conductor cable with hybrid sensor
- Single conductor wire with co-extruded sensor

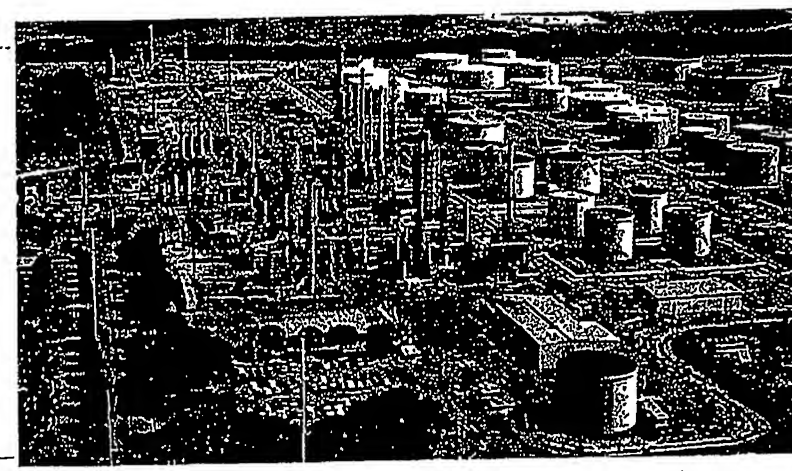




Other Applications

- Seals and gaskets
- Composite structures
- Boat hulls
- Plastic pipe
- Polymeric siding





REF. C

ShortWatch™

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Georgia Institute of Technology

An Electrical Condition Monitoring Approach for Wire and Cable -Based on Conductive Polymer Composite

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Ref (B)

Outline

- Introduction
- Objective
- Formulations and Test
- Results and discussion
- Conclusion

Ref (B)

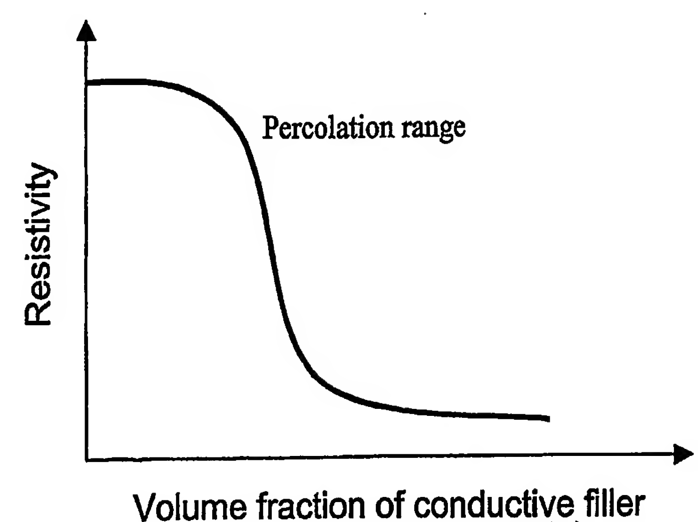
Introduction-Aging of cable

- Degradation reaction of polymer
  - Random chain scission (polyester)
  - Depolymerization (PMMA)
  - Crosslinking (PE)
  - Side group elimination (PVC)
  - Substitution (PE)
- Mechanisms of cable aging
  - Thermo-oxidation
    - Leads to a mixture of crosslinking and scission process,
    - Generates both oxidant product along the polymer chain such as ketones, aldehydes, acids, peroxides and alcohols) and gas product.
  - Radiation (especially for nuclear power plant cable)
- Properties change during aging process
  - Modulus ↑
  - Elongation to break ↓
  - Density ↑
    - Crosslinking
    - Substitution of hydrogen atoms with oxygen
    - Weight loss of polymer material (density of filler is higher than polymer resin)

Ref (B)

Introduction-conductive polymer composite

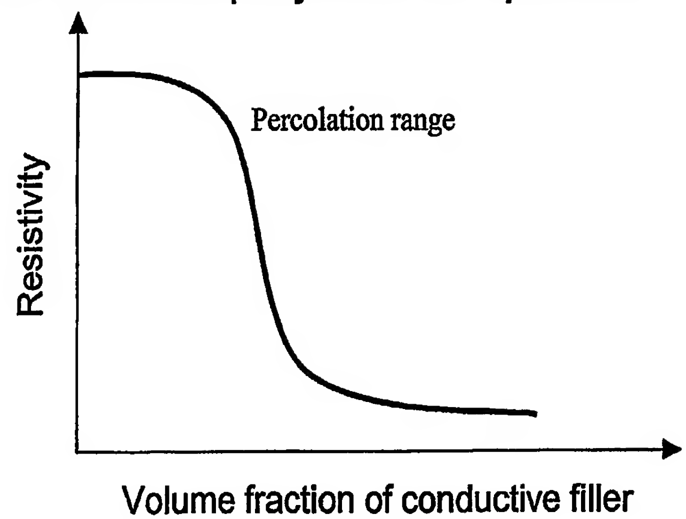
- Composition of conductive polymer composite
  - Conductive filler: metal, carbon black, graphite
  - Polymer matrix.
- Resistivity versus filler loading



Ref (B)

Objective

- To develop cable aging condition monitoring approach based on conductive polymer composite



Density increase ⇒ Volume fraction of conductive filler increase ⇒ Resistance decrease

Resistivity change is most sensitive to change of volume fraction of conductive filler when it is around percolation threshold.

Ref (B)

Materials Selection

- Polymer resin: EPR
  - To void complication of crystal during aging.
  - Density increased from 1.295 g/cm^3 to 1.360 g/cm^3 for EPR based cable materials during aging
  - Phase II: Other polymer matrix (PE, neoprene rubber, silicon rubber etc)
- Conductive filler-Carbon black
  - Relative wider percolation range than metal filler
  - It would be easier to obtain formulation with filler volume fraction around the percolation volume fraction.
  - Phase II: Metal filler (Ag, etc.)

Ref (B)

Formulations

EPDM: Royalene® 521 EPDM from Uniroyal Chemical, a terpolymer of ethylene, propylene and a non-conjugated diene (ENB).

Carbon Black: Vulcan XC-72 from Cabot

Name	EPDM	Carbon black	Clay	Crosslinker (methacrylate)	Resistivity (ohm-cm)
0%-CB	90	0	28	0.9	
10%-CB	90	10	18	0.9	
15%-CB	85	15	17	0.85	
20%-CB	80	20	16	0.8	
25%-CB	75	25	15	0.75	1.83×10^{7}
30%-CB	70	30	14	0.7	3.3×10^{4}

Sample thickness: 0.3-0.35 mm.

No antioxidant was added in the formulations

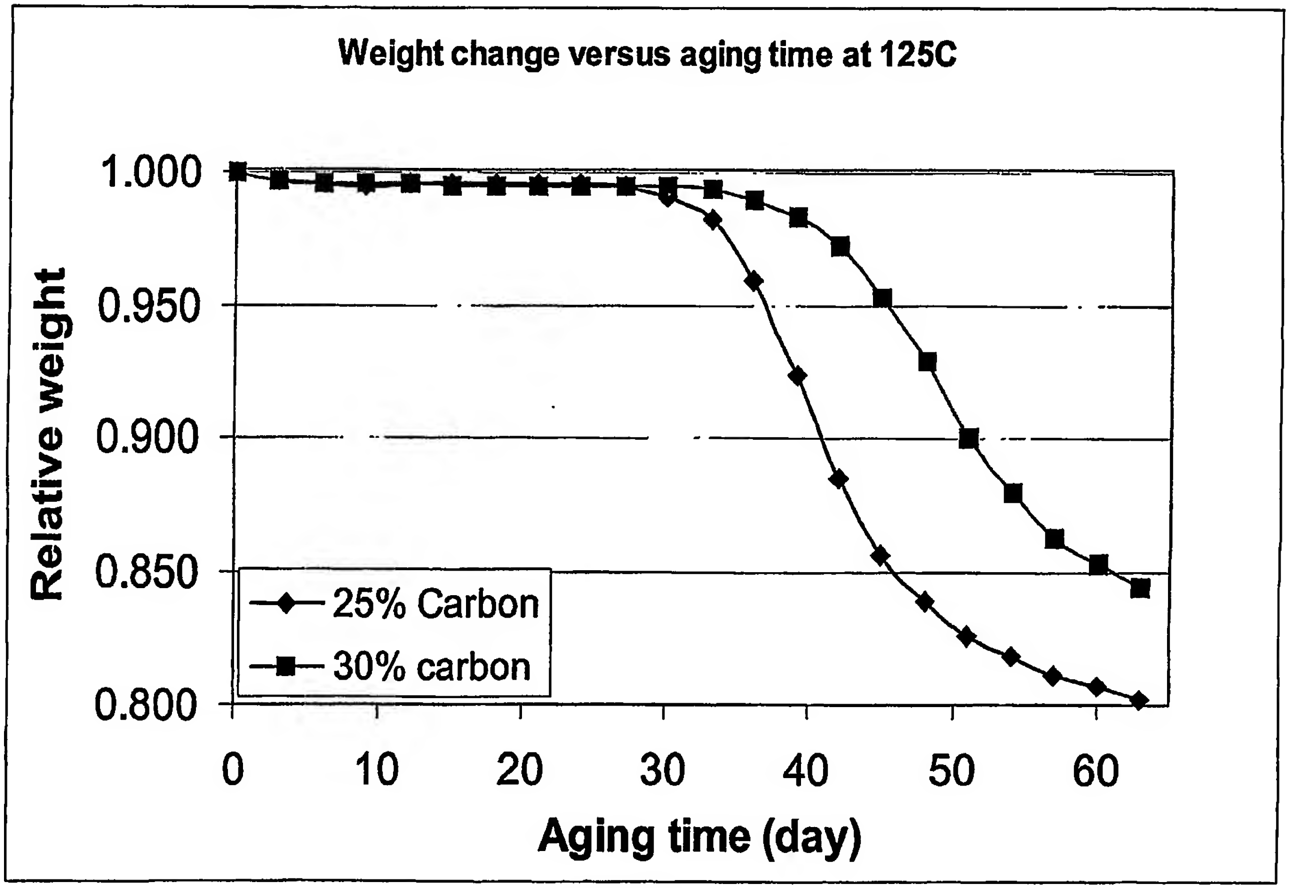
Antioxidant will be added in the formulations during Phase II

Ref (B)

Aging Condition and Properties Test

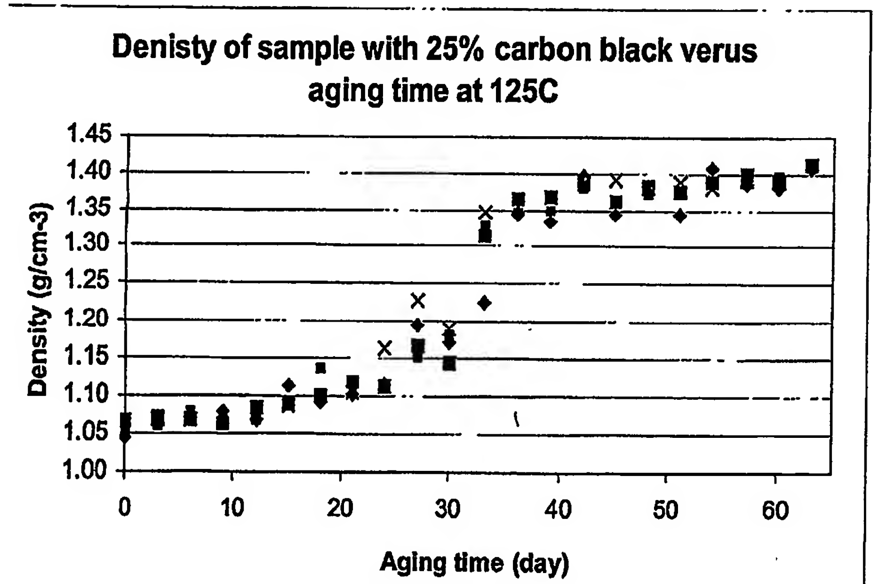
- Thermo-oxidation aging
  - 125°C in a convection oven (to avoid diffusion limited oxidation)
  - High temperature aging (150°C, 160°C)
- Radiation aging
  - 0.8 MRAD/hour
- Properties test
  - Weight
  - Density
  - Resistivity
  - Volume
  - Elongation at break Ref (B)

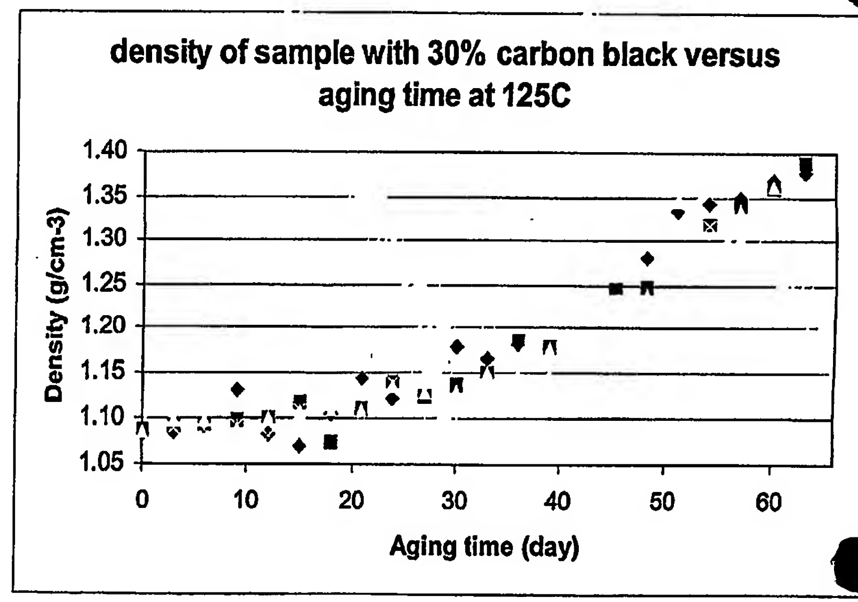
Weight Change during aging



Ref (B)

Density change during aging



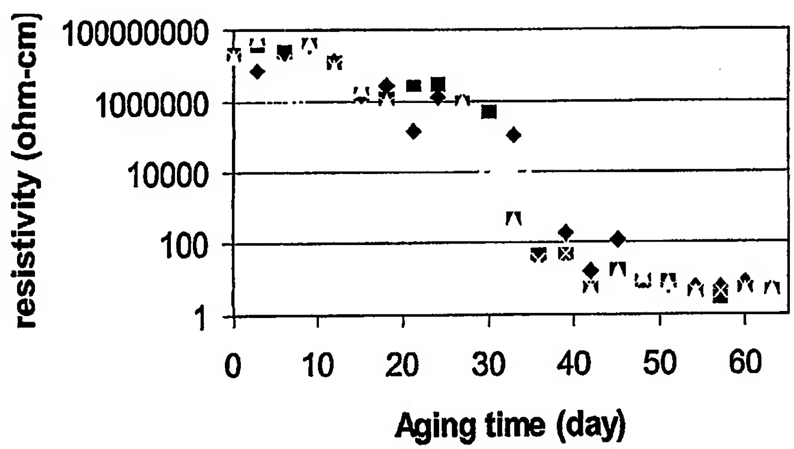


Density increased for 30% during the aging process

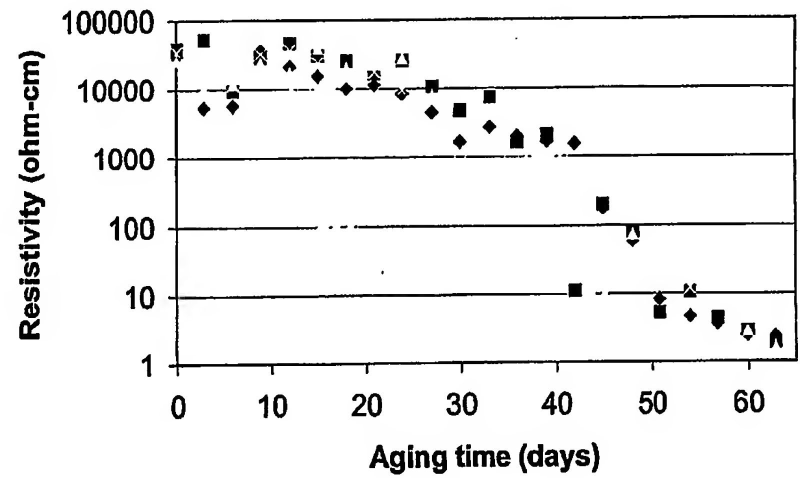
Ref (B)

Resistivity versus aging process

Restivitivity versus aging time for sample with 25% carbon black loading(aging temperaure: 125C, measured one day after the sample was taken out)



Resistivity versus aging time for sample with 30% carbon black loading (aging temperature: 125C, measured one day after the sample was taken out)

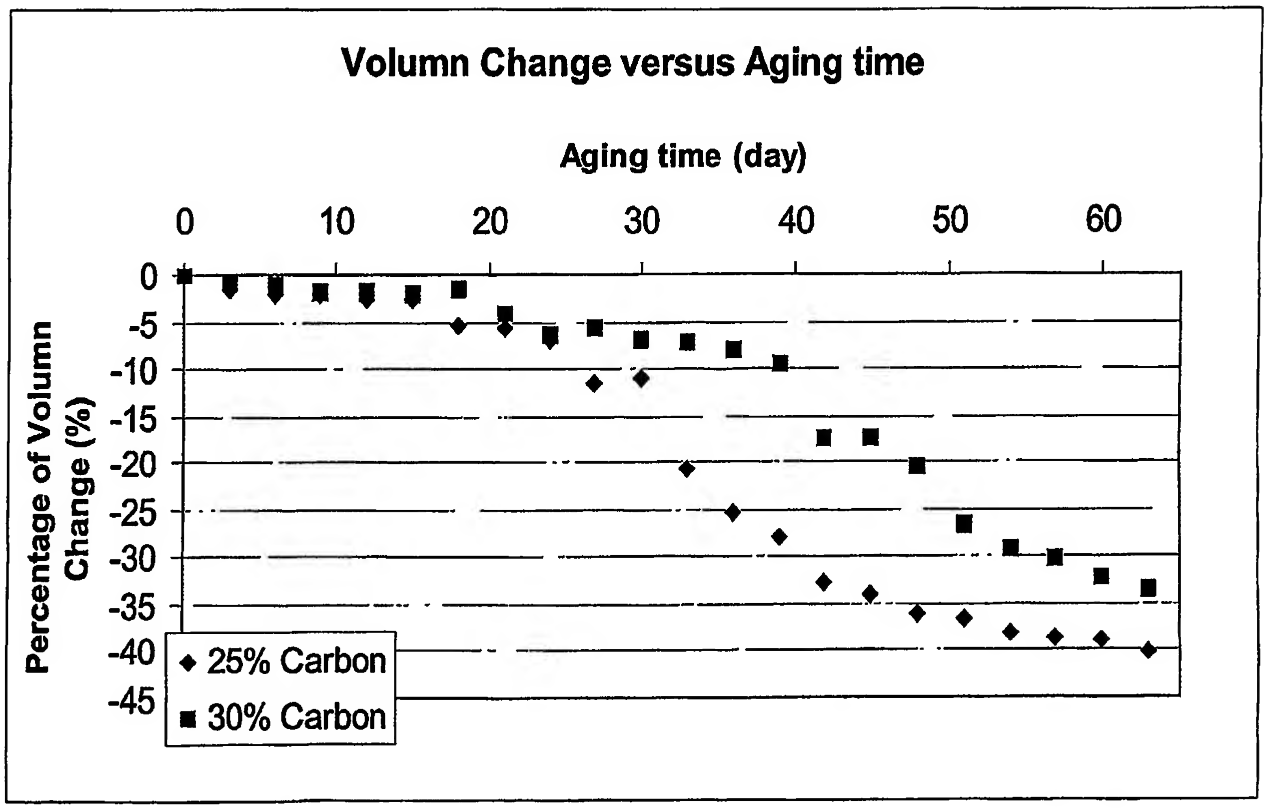


The resistivity decreased dramatically during aging. The difference was as high as 1000000 times for EPR+25%C.

The density change was amplified through the resistivity measurement!

Ref (B)

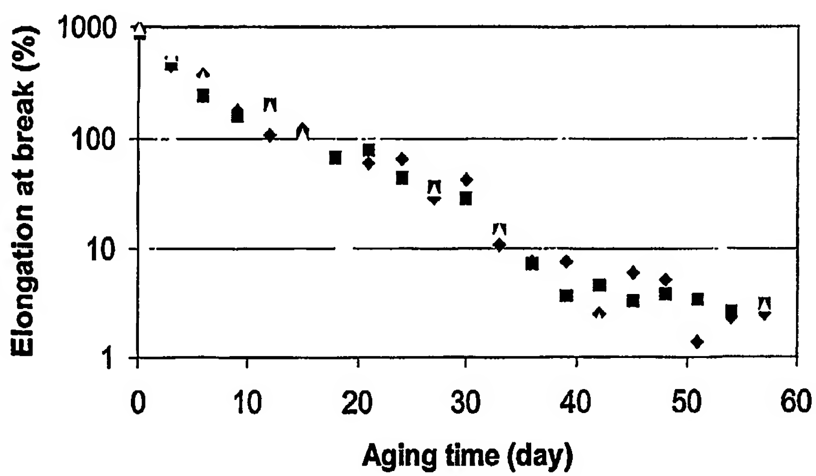
Volume change during aging at 125°C



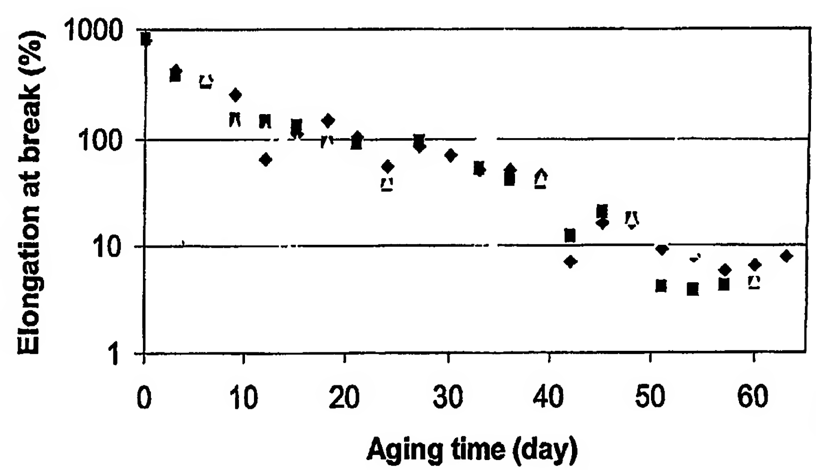
Ref (B)

Elongation at break after aging

Elongation at break versus aging time for sample with 25% carbon black

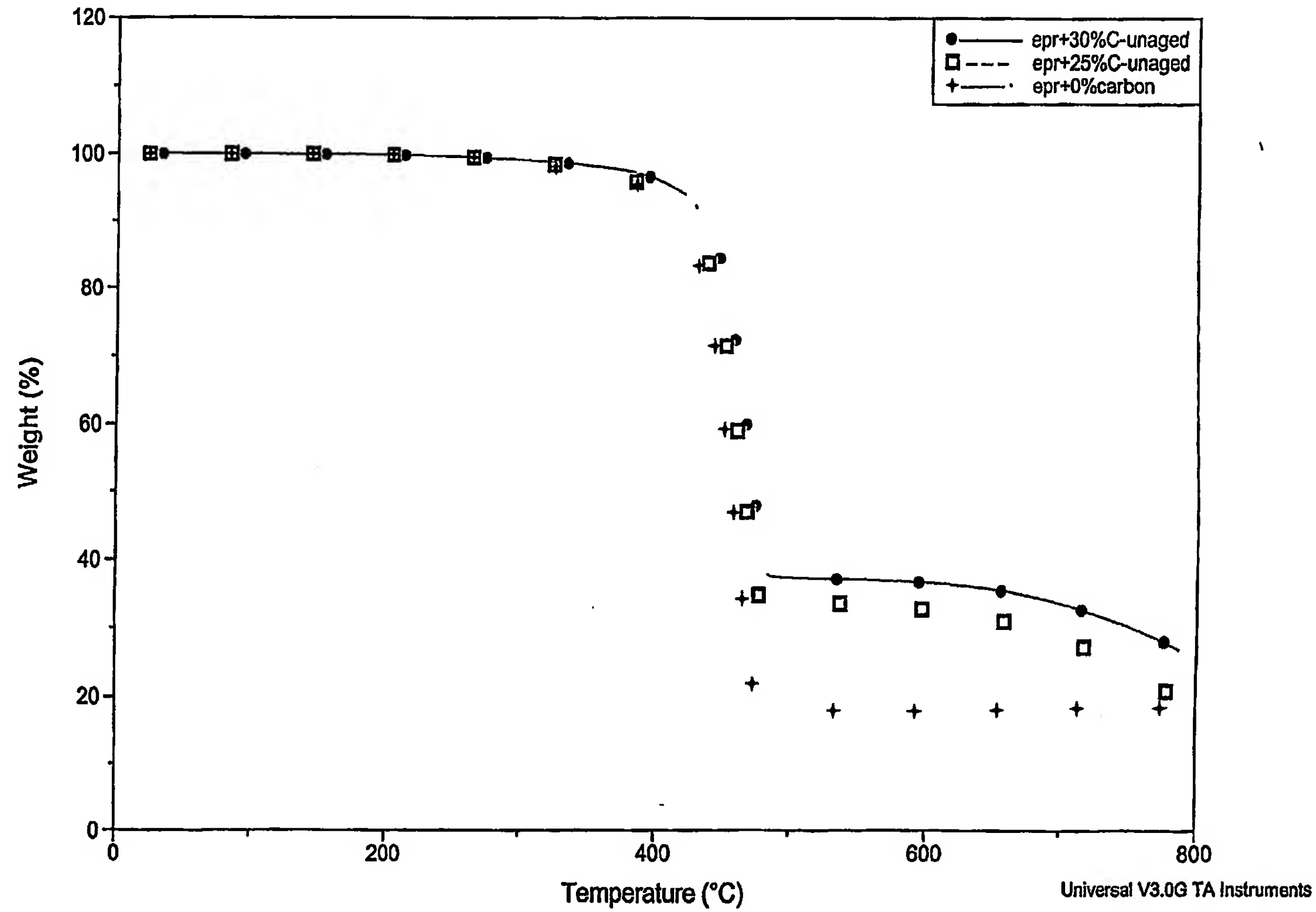


Elongation at break versus aging time for sample with 30% carbon black at 125C



Ref (B)

Thermal analysis of aging samples

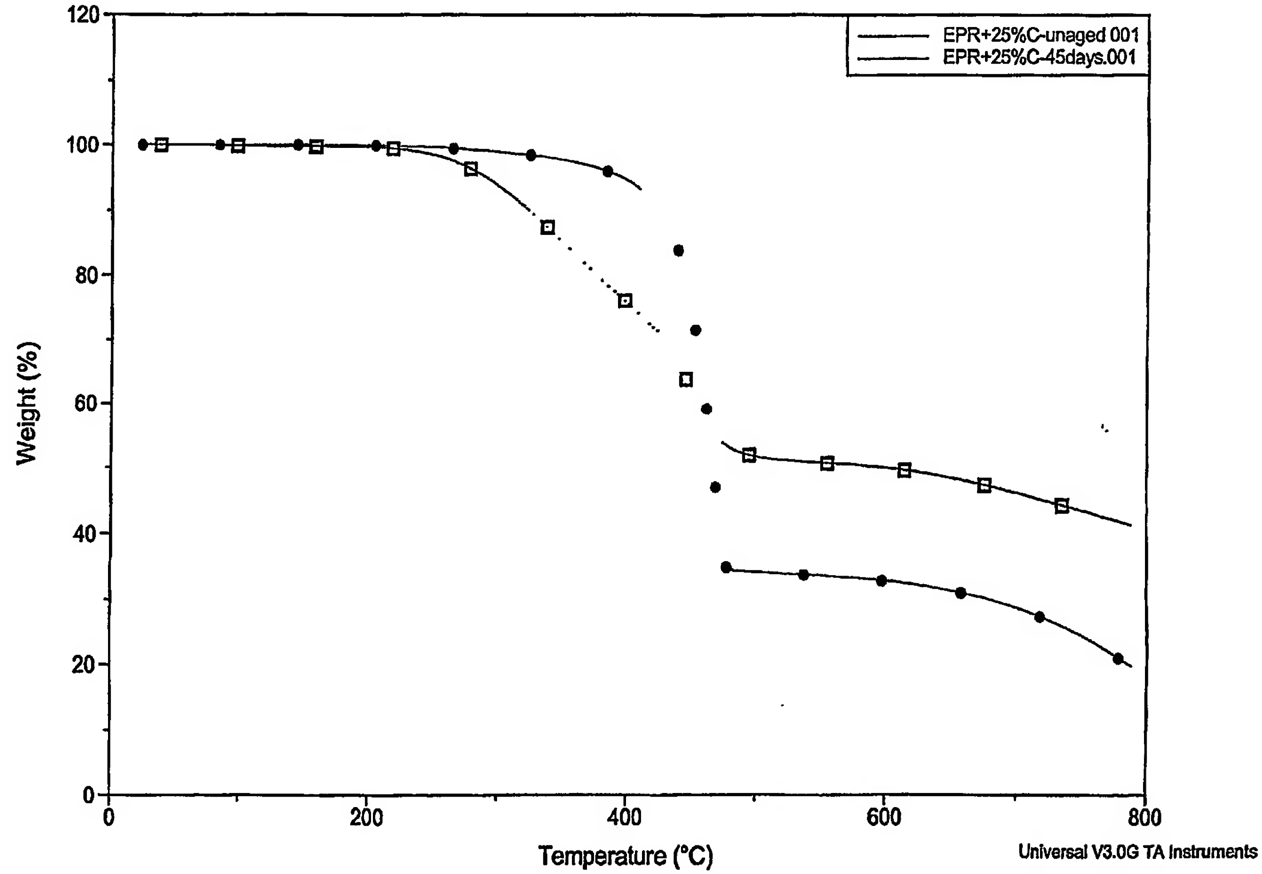


Ref (B)

TGA profiles of polymer composites before aging (under N_2, heating rate: 10°C/min)

Thermal analysis of the samples

TGA profiles of conductive polymer composites (with 25% carbon) before and after aging (under N_2, heating rate: 10°C/min)

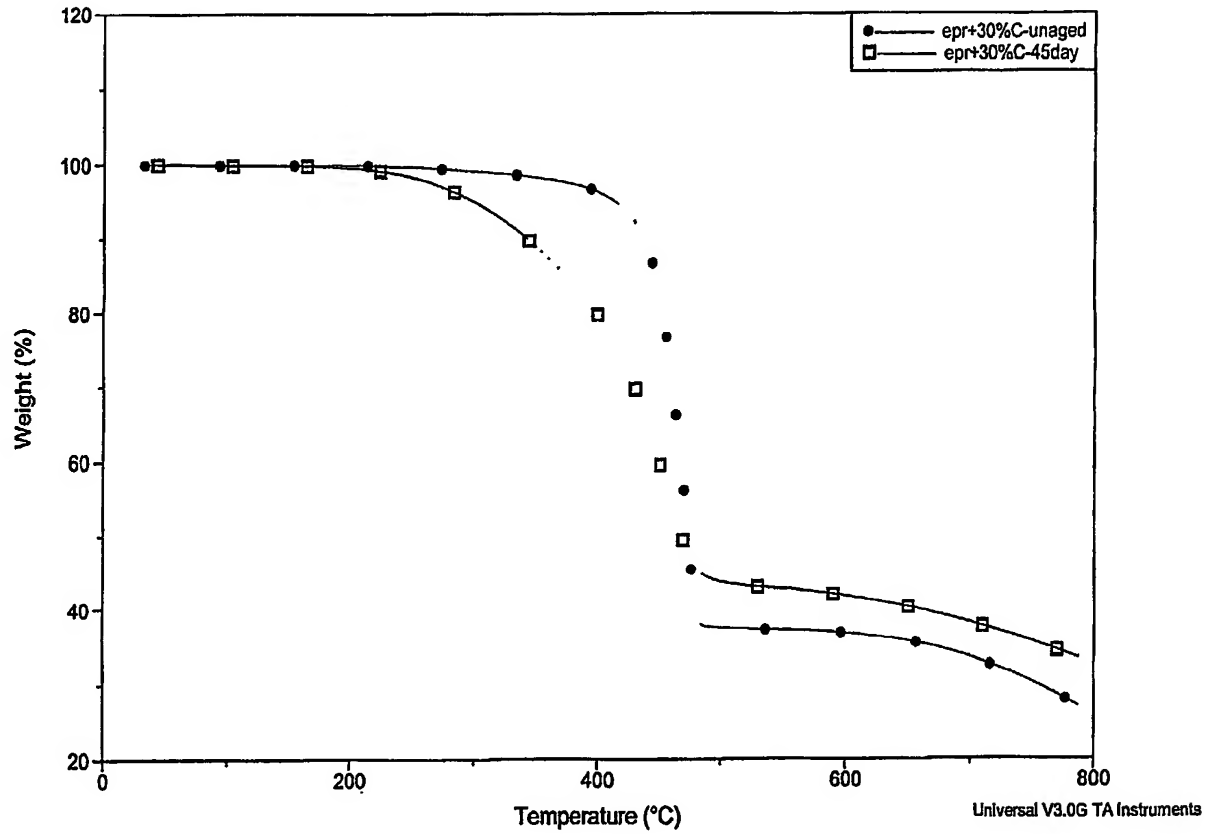


- **Decomposition temperature decreased after aging**
- **Residue increased due to loss of polymer resin during aging**

Ref (B)

Thermal analysis of aging samples

TGA profiles of conductive polymer composites (with 30% carbon) before and after aging (under N_2, heating rate: 10°C/min)



- Decomposition temperature decreased after aging
- Residue increased due to loss of polymer resin during aging

Ref (B)

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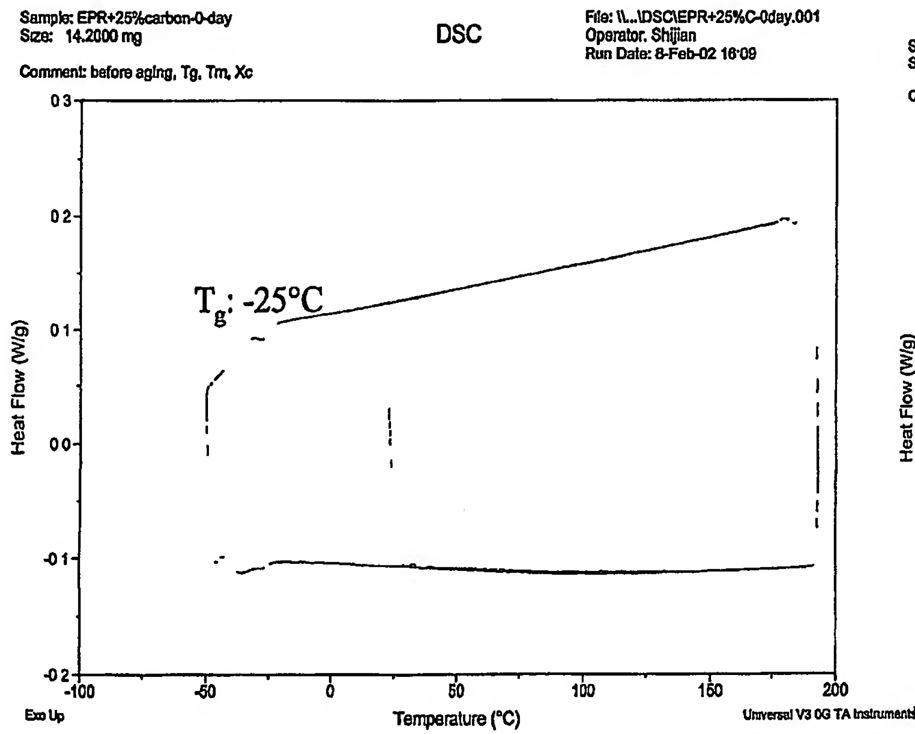
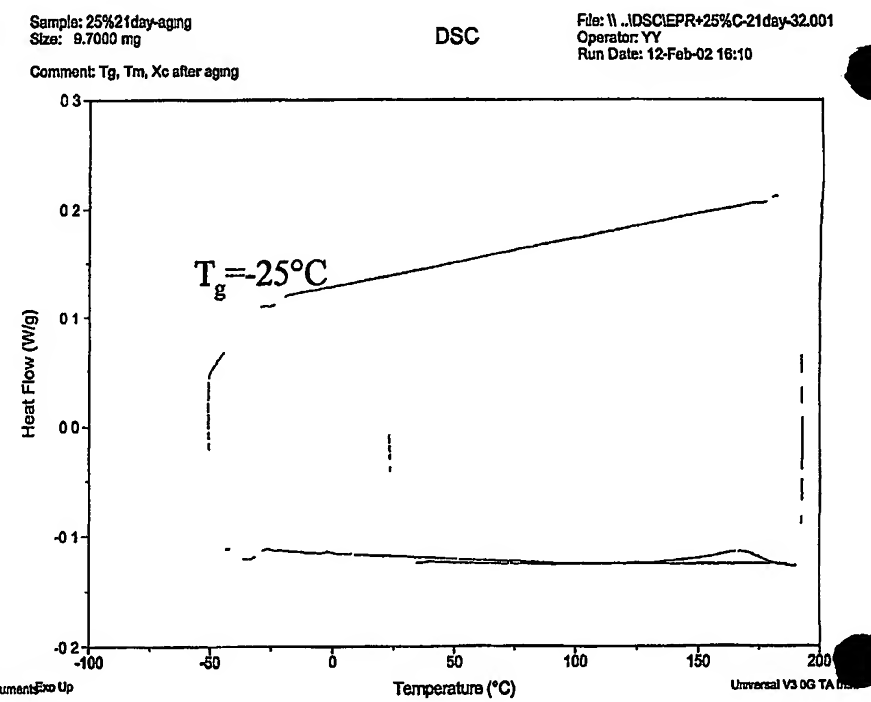
Thermal analysis of samples



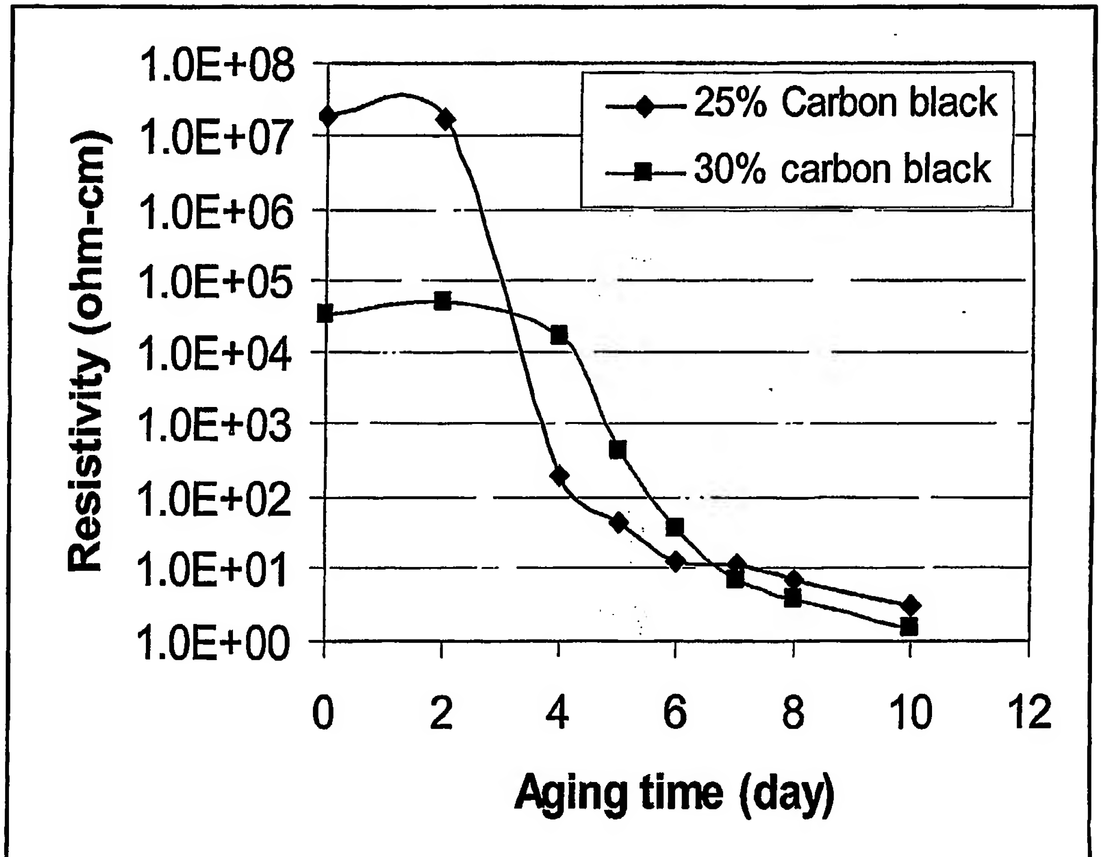


DSC profiles of samples before aging (left), after aging at 125C for 21 days (right). (Heating from room temperature to 200°C, cooling to –50°C, then heating to 200°C at 5°C/min under N_2.)

Ref (B)

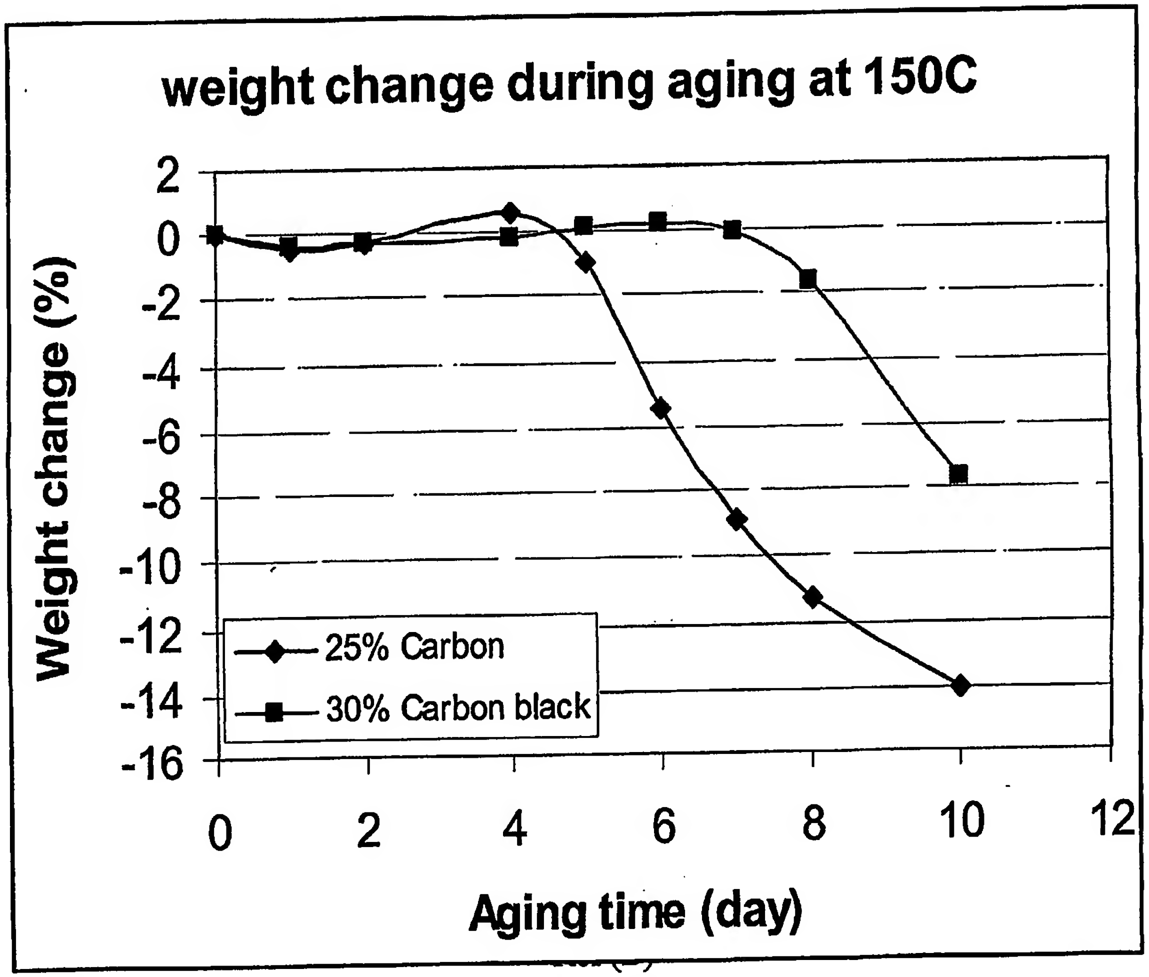
There is no crystallinity in the samples

Aging at 150°C

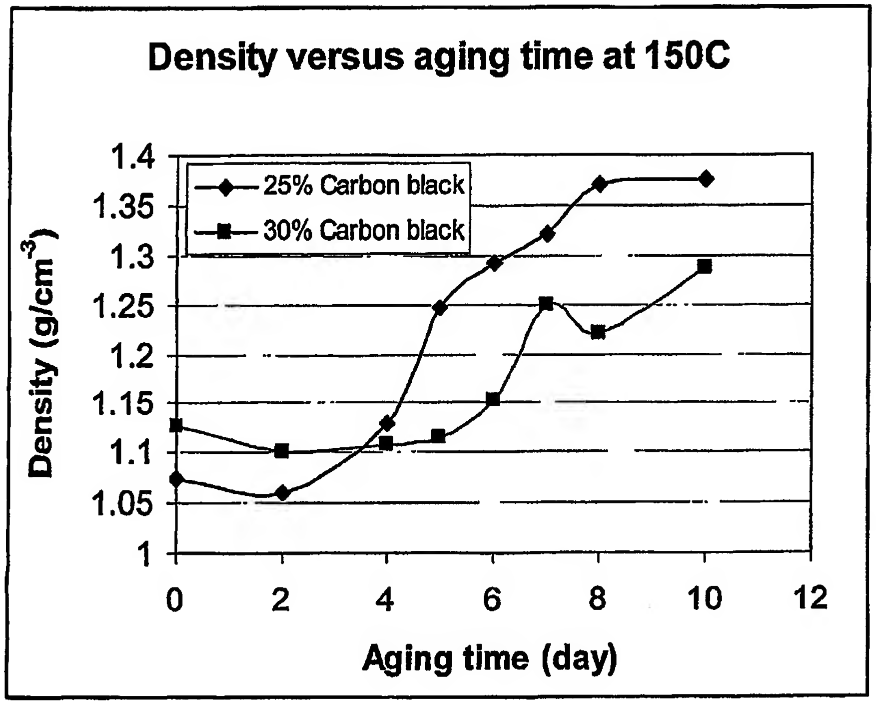


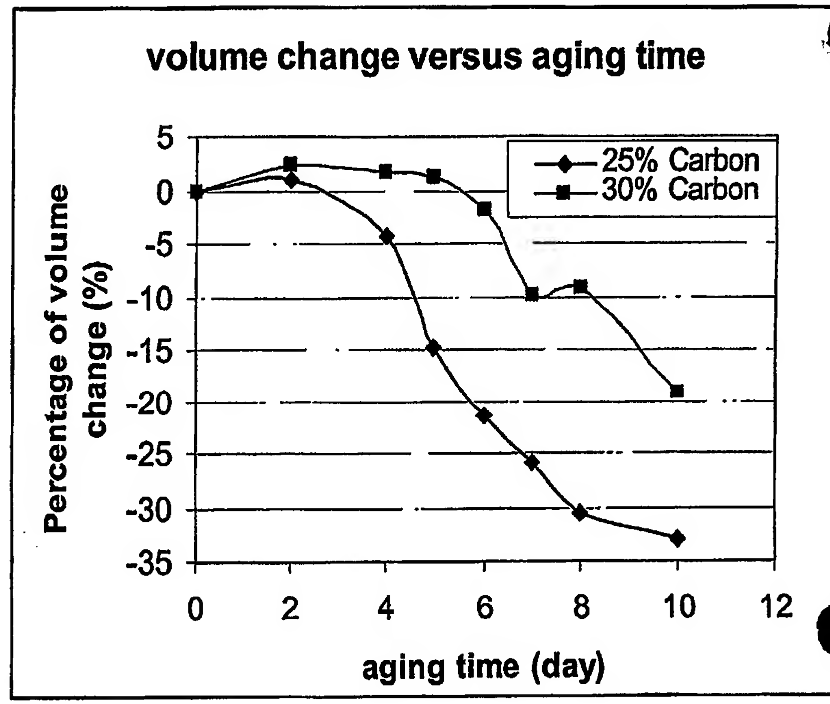
Resistivity versus aging time at 150C

Aging at 150°C



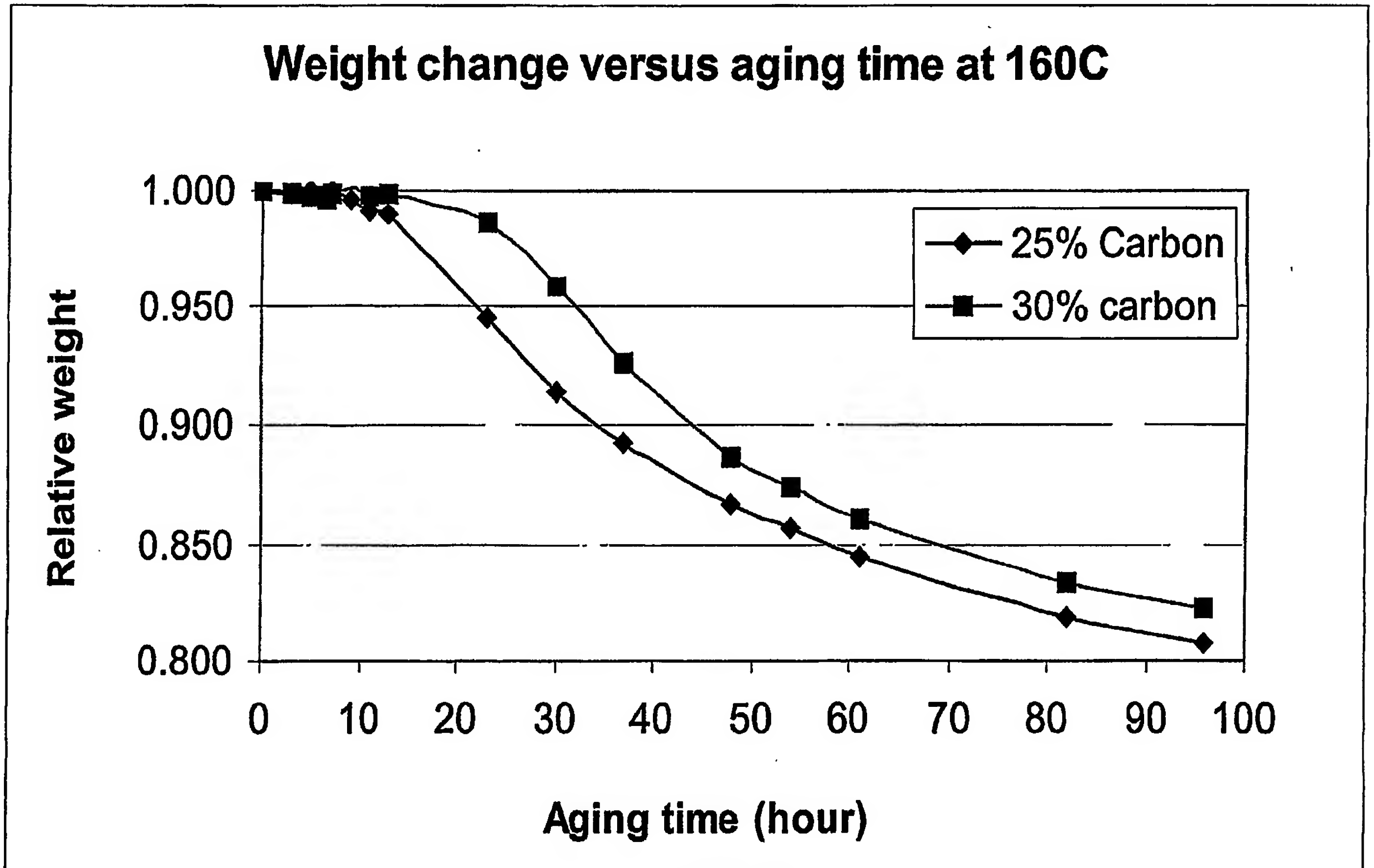
Aging at 150°C





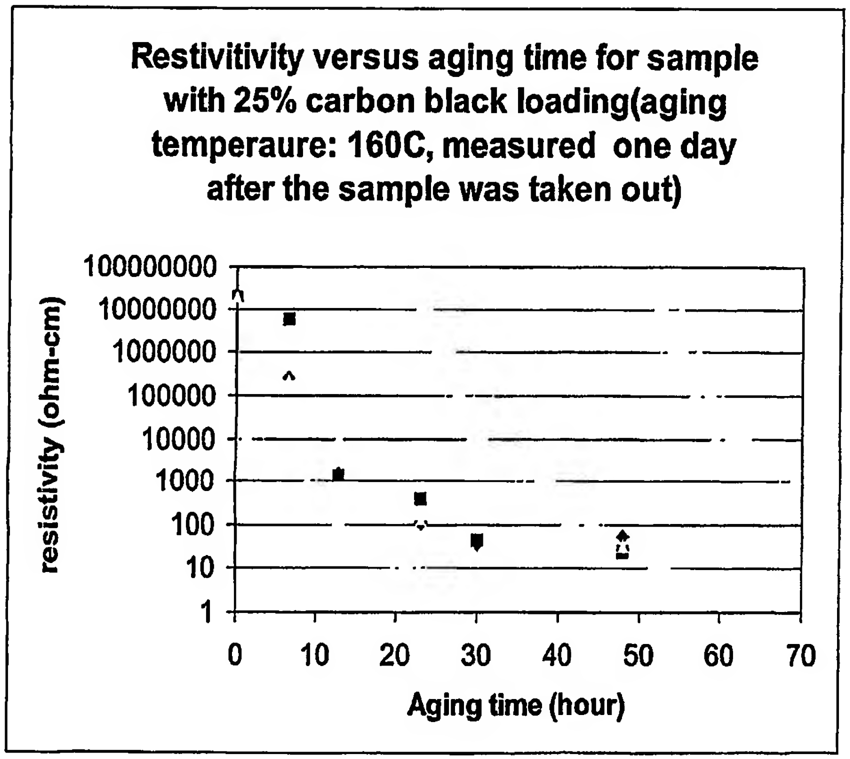
Ref (B)

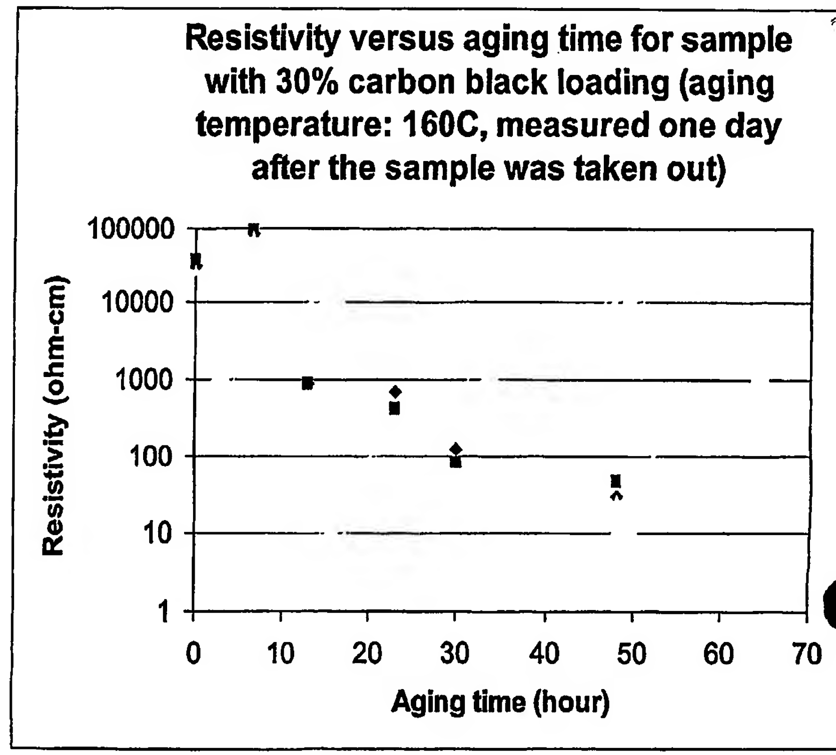
Aging at 160°C



Ref (B)

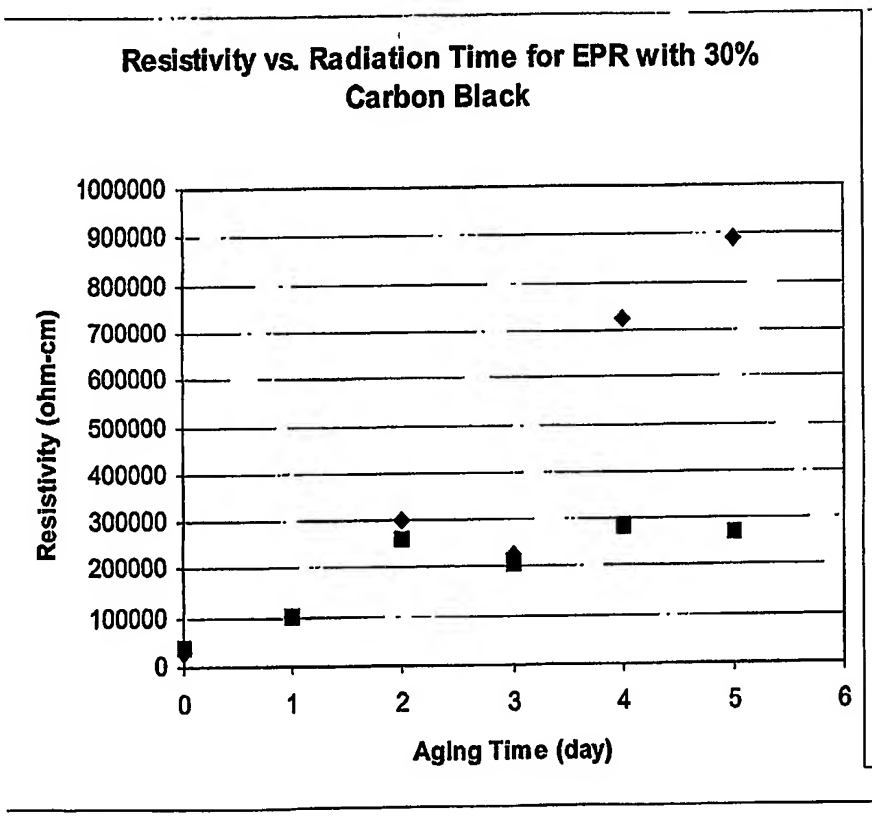
Aging at 160°C

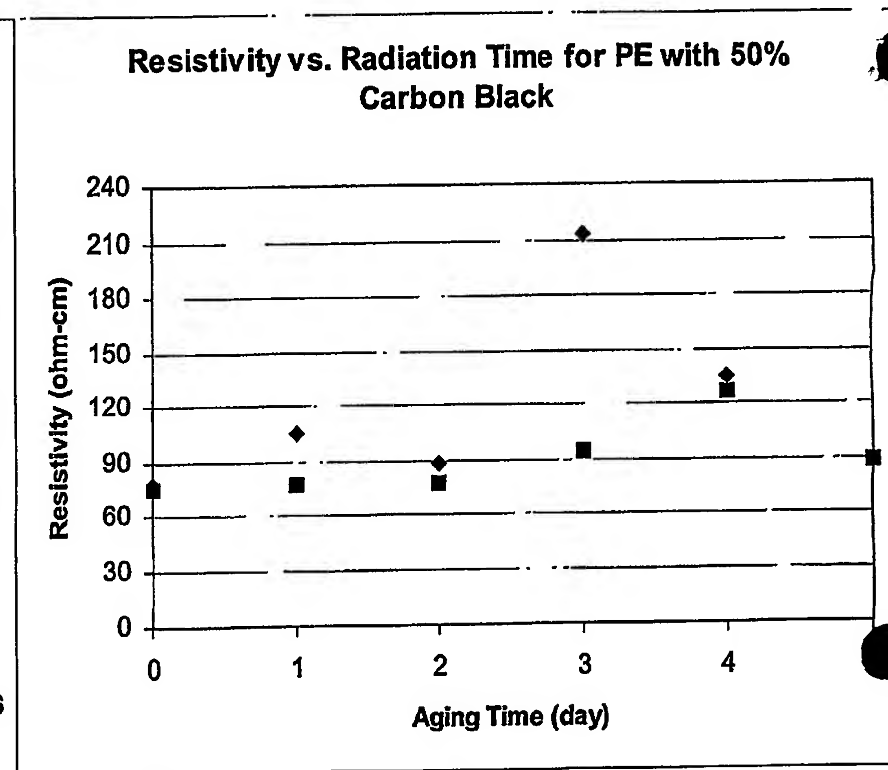




Ref (B)

Radiation aging





Ref (B)

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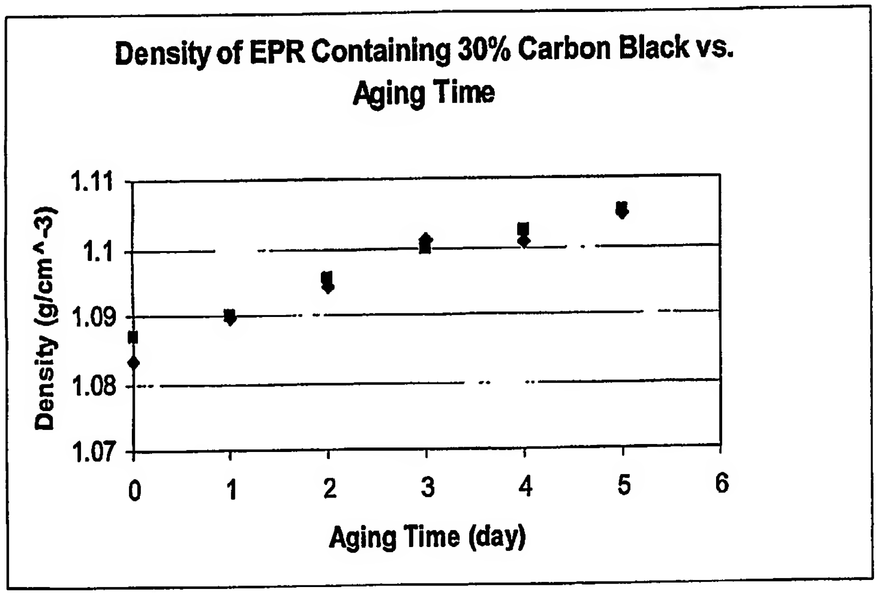
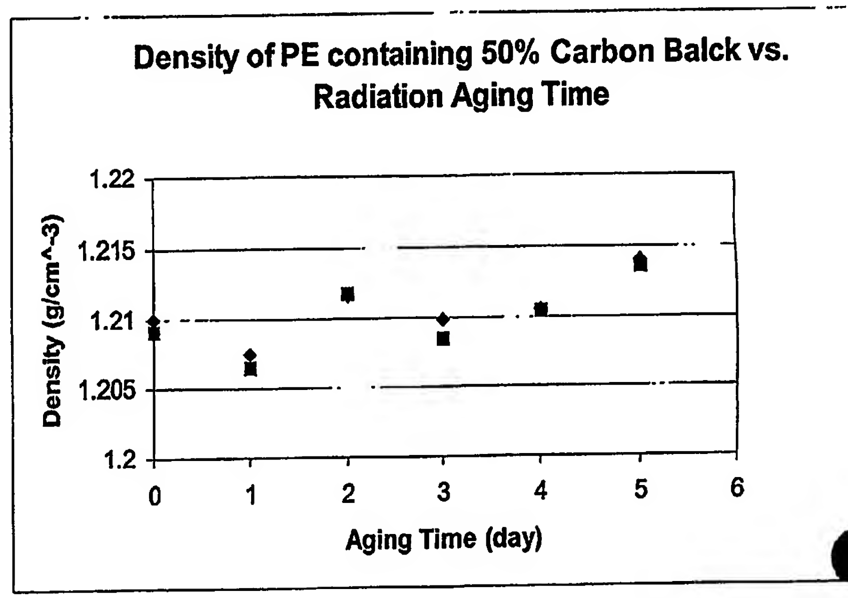
Radiation Aging





Ref (B)

Conclusions

- Density increased for 30% for EPR filled with carbon black (25%, 30%).
- Resistivity of carbon black filled EPR decreased dramatically during aging. The difference is as high as 1000000 times.
- Resistivity change of conductive polymer composite can be used to amplify the density change during aging, and thus monitor the aging of wire and cable
- Composite with more carbon black shows slower degradation

Ref (B)